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ERRATA.

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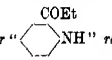
Page	Line	
110	10	*for* "coumarin" *read* "coumaran."
111	16	*for* "coumarin" *read* "coumaran."
120	11	*for* "" *read* "$CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot NH\end{smallmatrix}>CH\cdot CO\cdot CH_2\cdot CH_3$."

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ii, 237	15	*for* "26" *read* "12."

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ERRATA.

VOL. 117 (TRANS., 1920).

Page	Line	
646	26	*for* "Mr. E. A. Perren" *read* "Messrs. R. Craven and E. A. Perren."
646	27	*for* "his" *read* "their."
648	17	*for* "N/10-$KMnO_4$" *read* "N/10-$KMnO_4$ equivalent to."
648	20	*for* "0·03994" *read* "0·03004."

XL.—*Compounds of Thiocyanates of certain Bivalent Metals and Hydrazine.*

By PRIYADARANJAN RÂY and PULIN VIHARI SARKAR.

IT has already been shown (Curtius and Schrader, *J. pr. Chem.*, 1894, [ii], **50**, 311; Hofmann and Marburg, *Ber.*, 1897, **30**, 2019; Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1909, **60**, 247; Franzen and Lucking, *ibid.*, 1911, **70**, 145) that hydrazine gives compounds with various metallic salts similar to those formed by ammonia, and in the present paper compounds of hydrazine with the thiocyanates of nickel, cobalt, zinc, cadmium, and manganese are described. These compounds are closely related as regards their chemical and physical properties. They are all sparingly soluble in water, the nickel compound being the least soluble. Hence they have all been prepared by the addition of an ammoniacal hydrazine sulphate solution to the solution of any of the metallic salts in the presence of sufficient ammonium thiocyanate. The nickel and cobalt compounds possess very characteristic colours. They are all crystalline, and, with the exception of the nickel compound, all are decomposed by hot water into the corresponding metallic hydroxides; the manganese compound is immediately decomposed even by cold water, but in the presence of sufficient ammonium thiocyanate solution and hydrazine they can be preserved in cold water without any decomposition for a long time, air being carefully excluded in the case of the manganese compound. The nickel salt is very stable, and is not decomposed by boiling with water for a long time or by heating at 150° in the dry state. Cobalt stands next to nickel as regards stability. Judging from the marked change in the solubility of these compounds, and in the colour of the nickel and cobalt compounds, from those of their constituents, both the thiocyanates of the above metals and hydrazine being freely soluble in water, it can be safely asserted that complex ions are formed, and this has been conclusively proved by determining the conductivity of the nickel compound. The molecular conductivity was found to be 210·4, a value which indicates the presence of three ions and closely approaches those determined by Werner and Miolati (*Zeitsch. physikal. Chem.*, 1893, **12**, 34; 1894, **14**, 506) for complex ammonia salts of platinum, cobalt, and chromium. The values obtained by them for the molecular conductivity of those salts which yield two free ions in addition to the complex ion range from 234·4 to 267·6. The composition and

constitution of these compounds are therefore represented by the general formulæ $R(SCN)_2,2N_2H_4$ and $[R(N_2H_4)_2]^{\cdot\cdot}(SCN)'_2$, where R stands for Ni, Co, Zn, Cd, or Mn.

EXPERIMENTAL.

Compound of Nickel Thiocyanate and Hydrazine.—A solution of nickel sulphate was mixed with a concentrated solution of ammonium thiocyanate, and an ammoniacal solution of hydrazine sulphate was added. A voluminous violet-blue powder was precipitated, which was washed with water and dried in a vacuum. The substance is crystalline and very sparingly soluble in water, 100 grams dissolving 0·079 gram at 30°. It is not appreciably changed by cold dilute ammonia or acids, but on heating with the latter it decomposes and passes into solution, and with hot ammonia it becomes soluble, forming the blue nickel-ammonia cation:

0·1631 gave 0·0512 NiO. Ni = 24·7.

0·1097 „ (after oxidation with bromine) 0·2150 $BaSO_4$. S = 26·9.

0·0263, on treatment with alkaline ferricyanide (Rây and Sen, *Zeitsch. anorg. Chem.*, 1912, **76**, 380), gave 5·8 c.c. N_2 at 30° and 753·6 mm. N_2H_4 = 26·9.

$Ni(SCN)_2,2N_2H_4$ requires Ni = 24·6; S = 26·85; N_2H_4 = 26·85 per cent.

A solution of the substance in conductivity water was obtained by shaking for several hours at 24·5°. The resistance was found to be 1600 ohms. The strength of the solution was 0·0128 per cent., the cell constant 0·169, and hence the molecular conductivity = 210·4 at 24·5°.

Compound of Cobalt Thiocyanate and Hydrazine.—A solution of cobalt chloride was employed, and the same procedure was followed as in the case of the nickel compound. A voluminous, flesh-coloured powder was precipitated, which was washed with aqueous alcohol, then with absolute alcohol, and dried in a vacuum. The dry substance is fairly stable, decomposing at about 150° into black cobalt oxide. On heating with water, the substance decomposes, with the formation of cobaltous hydroxide. It is soluble both in dilute ammonia and dilute acids:

0·2511 gave 0·0623 Co. Co = 24·8.

0·1446 „ 0·2817 $BaSO_4$. S = 26·74.

0·0239 „ 5·3 c.c. N_2 at 30° and 750·06 mm. N_2H_4 = 26·9.

$Co(SCN)_2,2N_2H_4$ requires Co = 24·7; S = 26·8; N_2H_4 = 26·8 per cent.

Compound of Cadmium Thiocyanate and Hydrazine.—A concentrated solution of cadmium chloride was employed, and the same

procedure was followed as described above. A white, crystalline precipitate was obtained, which was collected, washed with alcohol, and dried in a vacuum. The substance decomposes into cadmium hydroxide on heating with water. It is soluble in dilute ammonia or dilute acids:

0·0563 gave 0·0404 $CdSO_4$. Cd = 38·6.

0·1346 „ 0·2139 $BaSO_4$. S = 21·81.

0·0541 „ 9·7 c.c. N_2 at 30° and 757·9 mm. N_2H_4 = 22·05.

$Cd(SCN)_2,2N_2H_4$ requires Cd = 38·44; S = 21·9; N_2H_4 = 21·9 per cent.

Compound of Zinc Thiocyanate and Hydrazine.—The same method of preparation was followed with a concentrated solution of zinc chloride. A white, crystalline precipitate was obtained, which was washed with alcohol and dried in a vacuum. On heating with water, the substance decomposes into zinc hydroxide. It is stable in the dry state, and soluble in dilute ammonia or dilute acids:

0·1520 (after oxidation with bromine and subsequent precipitation as basic carbonate) gave 0·0511 ZnO. Zn = 26·96.

0·0584 gave 0·1114 $BaSO_4$. S = 26·17.

0·0342 „ 7 c.c. N_2 at 27° and 760·5 mm. N_2H_4 = 25·7.

$Zn(SCN)_2,2N_2H_4$ requires Zn = 26·65; S = 26·1; N_2H_4 = 26·1 per cent.

Compound of Manganese Thiocyanate and Hydrazine.—A concentrated solution of manganese chloride was employed. The substance was obtained as a white, crystalline precipitate, which was washed with absolute alcohol and dried in a vacuum. It readily decomposes on contact with cold water, with the formation of brown, manganic hydroxide. In the dry state, the substance is fairly stable. It is soluble in dilute acids, and decomposes in the presence of dilute ammonia into manganic hydroxide:

0·1408 gave 0·0909 $MnSO_4$. Mn = 23·52.

0·1309 „ 0·2542 $BaSO_4$. S = 26·66.

0·0336 „ 7·25 c.c. N_2 at 28° and 761·7 mm. N_2H_4 = 27·19.

$Mn(SCN)_2,2N_2H_4$ requires Mn = 23·43; S = 27·2; N_2H_4 = 27·2 per cent.

Our best thanks are due to Prof. Sir P. C. Rây for his kind encouragement.

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[*Received, January 3rd, 1920.*]

XLI.—*Some Condensations of* n-*Butyl Alcohol and* n-*Butaldehyde.*

By Charles Weizmann and Stanley Frederick Garrard.

n-Butyl alcohol and *n*-butaldehyde are substances on which little work has been done beyond the preparation of the ordinary derivatives and the elucidation of their general properties.

n-Butyl alcohol is now, however, obtainable in large quantities, being a by-product in the new process for obtaining acetone, namely, by the fermentation of natural products containing starch by members of the group of organisms included under the generic name *Bacillus amylobacter.* The fermentation gives rise to acetone and *n*-butyl alcohol in the proportion of one part of acetone to two of *n*-butyl alcohol, together with a large volume of gas, consisting approximately of a mixture of equal volumes of hydrogen and carbon dioxide.

The production by this method of large quantities of *n*-butyl alcohol invited experimental work in a number of directions, and of these, the condensations of *n*-butyl alcohol and *n*-butaldehyde are not the least important.

n-Butaldehyde is readily obtainable from *n*-butyl alcohol by direct oxidation, but the yields are poor, being less than 30 per cent., most of the alcohol being converted into *n*-butyl *n*-butyrate and tarry matter.

The method adopted to prepare *n*-butaldehyde in quantity was that of Bouveault, using a copper catalyst at 300°, an almost theoretical yield of aldehyde from alcohol being obtained.

n-Butaldehyde readily undergoes the "aldol" condensation giving a 60—70 per cent. yield of the aldol,

$$OH{\cdot}CHPr^{\alpha}{\cdot}CHEt{\cdot}CHO,$$

which on distillation under the ordinary pressure loses water, giving α-ethyl-Δ^{α}-hexenealdehyde, $CHPr^{\alpha}{:}CEt{\cdot}CHO$, and this, on complete reduction with aluminium amalgam and water, gives α-ethylhexyl alcohol, $CH_2Pr^{\alpha}{\cdot}CHEt{\cdot}CH_2{\cdot}OH$.

On oxidation with silver oxide and barium hydroxide, α-ethyl-Δ^{α}-hexenealdehyde gives an unsaturated acid, $CHPr^{\alpha}{:}CEt{\cdot}CO_2H$, which on reduction with zinc and sulphuric acid gives α-ethylhexoic acid, $CH_2Pr^{\alpha}{\cdot}CHEt{\cdot}CO_2H$.

Guerbet, in his work on the action of sodium on alcohols (*Compt. rend.*, 1901, **133**, 1220; 1902, **134**, 467), obtained from *n*-butyl alcohol an octyl alcohol, in every way similar to the above, to

which he gave the formula $CH_2Pr^{\alpha}\cdot CHMe\cdot CH_2\cdot OH$. This would obviously be formed by the loss of water from two molecules, thus: $CH_2Pr^{\alpha}\cdot\boxed{OH\ \ H}CHMe\cdot CH_2\cdot CH_2\cdot OH$, that is, it is the β-hydrogen atom that reacts. This seems improbable, owing to the superior activity of α-hydrogen atoms, and the reaction was investigated in order to discover the best conditions and also to establish the constitution of the octyl alcohol obtained.

The production of *n*-butyric acid by the interaction of *n*-butyl alcohol and sodium led to the investigation of the action of sodium hydroxide on *n*-butyl and ethyl alcohols.

The action of sodium on mixed *n*-butyl and ethyl alcohols was also tried, with results similar to those obtained with *n*-butyl alcohol, but with poor yields.

Action of Sodium on n-*Butyl Alcohol.*—Experiments were carried out with varying amounts of sodium and at varying temperatures. The products consisted of octyl alcohol, *n*-butyric acid, and some octoic acid, with traces of esters, ethers, and dodecyl alcohol.

In all cases, the amounts of octyl alcohol and *n*-butyric acid were proportional to the actual amount of sodium present, within small limits. The temperature at which the reaction was carried out had no effect, except on the time required to complete the reaction.

The equation which represents the reaction is as follows:

$$3C_4H_9\cdot OH + Na \longrightarrow C_8H_{17}\cdot OH + C_4H_7O_2Na + 5H.$$

Some of the *n*-butyric acid was always replaced by a little octoic acid, and similarly some *n*-butyl alcohol was always found unchanged.

The reaction evidently takes place in two stages, namely, (i) formation of octyl alcohol and sodium hydroxide,

$$C_4H_9\cdot OH + C_4H_9\cdot ONa = C_8H_{17}\cdot OH + NaOH,$$

and (ii) formation of acid from alcohol.

The sodium hydroxide formed in (i) then acts on unchanged *n*-butyl alcohol, giving *n*-butyric acid and hydrogen,

$$C_4H_9\cdot OH + NaOH = C_4H_7O_2Na + 4H.$$

The octoic acid obtained, and consequently the octyl alcohol, has the α-ethyl, and not the β-methyl, structure assigned to it by Guerbet. The constitution was established by a comparison of the amide with that of α-ethylhexoic acid prepared by Raper's method (T., 1907, **91**, 1837).

Action of Sodium Hydroxide on n-*Butyl and Ethyl Alcohols.*—This reaction is almost identical with the second part of the above reaction. In the case of *n*-butyl alcohol, about 80 per cent. of the sodium hydroxide is converted into sodium *n*-butyrate when excess

of alcohol is used, small quantities of α-ethylhexyl alcohol and α-ethylhexoic acid being also formed.

The action of sodium hydroxide on ethyl alcohol gives only poor yields of acetic acid, quantities of a brown, resinous substance being obtained, which appears to be akin to aldehyde resin.

The action of metallic calcium on *n*-butyl alcohol is similar to that of sodium, smaller yields of α-ethylhexyl alcohol being obtained, but very little *n*-butyric acid. This is borne out by the fact that calcium oxide and slaked lime when heated with *n*-butyl alcohol give only negligible quantities of *n*-butyric acid.

Action of Sodium on a Mixture of n-*Butyl and Ethyl Alcohols.*—A few experiments only were carried out, as the yields were poor, less than 20 per cent. of *n*-hexyl alcohol and *n*-hexoic acid being obtained.

The products were mainly α-ethylhexyl alcohol and *n*-hexoic acid, in addition to *n*-butyric acid. Very little *n*-hexyl alcohol was obtained. Other products were acetic acid and α-ethylhexoic acid.

The hexoic acid and hexyl alcohol have a normal chain of six atoms, and must therefore be formed thus:

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\boxed{ONa \quad H}CH_2{\cdot}CH_2{\cdot}OH.$$

This points to the fact that when sodium is dissolved in a mixture of the alcohols, or when sodium ethoxide is dissolved in *n*-butyl alcohol, most of the sodium is present as *n*-butoxide and not as ethoxide. This bears out recent work on solutions of sodium hydroxide in ethyl alcohol, which are stated to contain most of the sodium as ethoxide.

The yields obtained here, although poor, were better than those obtained by Guerbet (*Compt. rend.*, 1902, **135**, 172) from heptyl and ethyl alcohols, in which case the yields of nonyl alcohol were only 3—5 per cent.

α-Ethylhexyl alcohol is readily dehydrated by heated aluminium oxide, giving theoretical yields of an *octylene*. This, when shaken with 90 per cent. sulphuric acid, gives a pleasant-smelling hydrocarbon having the same empirical formula, which is probably a *dioctylene*.

Condensations of n-*Butaldehyde and* n-*Butyl Alcohol with Acetone.*—*n*-Butaldehyde readily condenses with acetone when treated with alkali hydroxides. With 10 per cent. potassium hydroxide it gives an aldol, $OH{\cdot}CHPr^{\alpha}{\cdot}CH_2{\cdot}COMe$, which on distillation gives *Δ^{γ}-heptylene-β-one* (n-*butylideneacetone*),

$$CHPr^{\alpha}{:}CH{\cdot}COMe.$$

By passing *n*-butaldehyde and acetone over aluminium oxide, some *n*-butylideneacetone was obtained, but the main products were hydrocarbons of low boiling points.

n-Butylideneacetone undergoes changes when heated with sodium hydrogen sulphate or sulphuric acid, and when passed over heated copper, which suggests the formation of ring compounds, but no definite results have been obtained at present.

n-Butyl alcohol and acetone when passed over heated aluminium oxide lose water, giving a complex mixture of products from which methyl amyl ketone and a *heptadiene*, C_7H_{12}, have been isolated; traces of *n*-butaldehyde and *iso*propyl alcohol are also present.

Other products are probably an unsaturated alcohol, isomeric with methyl amyl ketone, and the hydrocarbon derived from it, possibly allylene or allene, and other hydrocarbons and various oils of high boiling points which have not been identified.

The reaction is probably mainly $CH_2Pr^{\alpha}\cdot\boxed{OH \quad H}CH_2\cdot COMe$, giving methyl amyl ketone, and $CMe_2\boxed{O \quad H_2}CEt\cdot CH_2\cdot OH$, giving an unsaturated alcohol, both the ketone and alcohol undergoing further dehydration, yielding hydrocarbons.

Experimental.

n-*Butyl Alcohol.*

Starch, and carbohydrates in general, when fermented by members of the group *Bacillus amylobacter*, give rise to acetone and *n*-butyl alcohol.

About 25 per cent. of the starch is lost as a mixture of hydrogen and carbon dioxide in equal proportions, and about 25 per cent. is found in the fermented "wash" as acetone (8—9 per cent. on the starch) and *n*-butyl alcohol (16—17 per cent. on the starch), together with a little *iso*propyl alcohol, probably formed by the reduction of some of the acetone by the hydrogen present. The bacillus is anærobic, the fermentation being complete in from twenty-four to thirty hours, according to conditions. Traces of acid are formed, which suggests that hydroxybutyric acid is an intermediate product.

The fermented "wash" is distilled, and the "oil" salted out from the distillate with potassium carbonate; on distillation, the oil is fractionated as below:

Typical Distillation of 500 *Grams of "Oil."*

55—60°	126 grams	85— 90°	4 grams.
60—65	2 ,,	90— 95	58 ,,
65—70	1 ,,	95—110	3·5 ,,
70—75	1 ,,	110—115	nil
75—80	9 ,,	115—120	250 grams.
80—85	2 ,,		

The 90—95° fraction consists mainly of a mixture of water and *n*-butyl alcohol, which separates into two layers on cooling, the alcohol layer containing 19 per cent. of water and the aqueous layer 18 per cent. of alcohol.

The mixture boils at 91° and contains 35 per cent. of water.

In order to purify the *n*-butyl alcohol thus obtained, it was distilled over 1—2 per cent. of calcium, the fraction 116—117° being collected.

iso*Propyl Alcohol.*—In the identification of this alcohol in the oil, a few points of interest occurred.

After careful drying and distillation from solid sodium hydroxide, the alcohol was found to boil at 78—79°, and not at 83°, which is the value usually given.

The phenyl carbamate, after repeated recrystallisation from light petroleum, melted at 75—76° (Gumpert, *J. pr. Chem.*, 1885, [ii], **32**, 279, gives 90°, and Spica and de Varda, *Gazzetta*, 1887, **17**, 165, gave 42—43°). The phenylcarbamates of *n*-butyl and ethyl alcohols were found to melt at 61° and 51° respectively.

n-*Butaldehyde.*

(*a*) *By Direct Oxidation of* n-*Butyl Alcohol.*—The oxidation mixture used for the conversion of *iso*butyl alcohol into *iso*butaldehyde (Fossek, *Monatsh.*, 1881, **2**, 614) proved to be unsuitable for this preparation, and the following method of preparation was adopted.

Into 200 grams of *n*-butyl alcohol heated to 90—100°, a mixture of 200 grams of sodium dichromate, 180 grams of sulphuric acid, and 450 grams of water was slowly dropped at such a rate that there was continual ebullition. *n*-Butaldehyde, *n*-butyl alcohol, and *n*-butyl *n*-butyrate distilled over, and, after being dried, were separated by distillation. In three experiments, 58, 55, and 56 grams of *n*-butaldehyde were obtained, most of the alcohol being converted into *n*-butyl *n*-butyrate and tarry matter.

If the alcohol is dropped into the oxidation mixture, only traces of aldehyde are obtained.

Oxidation with ammonium persulphate, using cerium oxide as catalyst, gave only traces of *n*-butaldehyde.

(*b*) *Catalytic Method.*—The method employed was that of Bouveault (*Bull. Soc. chim.*, 1908, [iv], **3**, 118), in which carefully reduced copper hydroxide, suspended on copper gauze heated to 300°, is used as catalyst.

If care is taken, the catalyst does not deteriorate, although traces of *n*-butyric acid appear to be formed. The yield is theoretical,

and about 50—100 grams per hour can be obtained from a "catalyser" 45 cm. × 1·9 cm.

If the catalyst is heated to 400°, further dehydrogenation takes place, and some crotonaldehyde is obtained in addition to *n*-butaldehyde.

α-Ethyl-Δ^α-hexenealdehyde.

This was prepared by a modification of Raupenstrauch's method (*Monatsh.*, 1887, **8**, 108).

n-Butaldehyde (20 grams) and ether (10 c.c.) were mixed with a quantity of 10 per cent. aqueous potassium hydroxide, the whole was shaken for two hours, and allowed to remain for fifteen hours. The product was then washed with dilute sulphuric acid and water, dried, and distilled. On distillation, water was eliminated quantitatively from the aldol, giving the aldehyde boiling at 172—173°/760 mm.

The results with varying amounts of 10 per cent. potassium hydroxide solution were as follows, 20 grams of *n*-butaldehyde being used in each case:

Ten per cent. potassium hydroxide. c.c.	Product, b. p. 150—180°. Grams.	Yield. Per cent.
0·5	A few drops only	—
1·0	4	23
2·0	11	63
3·0	11·5	66
4·0	12·7	71
5·0	10·5	60

Other experiments, using 1 c.c. of the potassium hydroxide solution to 5 grams of *n*-butaldehyde, gave the following results:

Butaldehyde. Grams.	Yield. Per cent.
80	71·2
40	67·5
100	68·0

The *semicarbazone* melts at 132°.

In addition to a 70 per cent. yield of the "aldol," some of the *n*-butaldehyde is recovered unchanged, and some is converted into a substance boiling above 180°, which is probably identical with the unsaturated aldehyde, $C_{12}H_{22}O_2$, described by Gorhan (*Monatsh.*, 1905, **26**, 73).

α-Ethylhexyl Alcohol.

To 37 grams of α-ethyl-Δ^α-hexenealdehyde 16 grams of amalagamated aluminium and 200 c.c. of water were added, and

the mixture was allowed to remain for four days with occasional shaking. It was then distilled in a current of steam until no more oil passed over, and the distillate boiled under reflux for two hours with 5 grams of sodium hydroxide to remove any unreduced aldehyde as resin. The mixture was then distilled in a current of steam, and the alcohol extracted from the distillate with ether, the solution dried, evaporated, and distilled, the fractions 175—195° being collected; on redistillation, 10 grams of α-ethylhexyl alcohol boiling at 180—185° were obtained.

α-Ethylhexoic Acid.

The acid corresponding with the above alcohol was obtained as follows. Thirty grams of the aldehyde were mixed with the silver oxide, obtained by adding the theoretical quantity of barium hydroxide to 90 grams of silver nitrate. This mixture was treated with 600 c.c. of *N*/2-barium hydroxide solution, a few c.c. at a time, the whole being kept cold and vigorously shaken. It was then allowed to remain for twelve hours. Excess of barium hydroxide was removed by means of carbon dioxide, and the clear solution acidified with sulphuric acid. The free acid was extracted with ether, the solution dried, evaporated, and distilled, the fraction 165—175° being collected. The crude, unsaturated acid was heated for twelve hours on the water-bath with a large excess of zinc and sulphuric acid. The reduced acid was extracted with ether, and ultimately 15 grams of an acid boiling at 225° (the fraction 220—226° was collected) were obtained.

The amide melted at 101·5°, and this melting point was not changed when the substance was mixed with the amide of α-ethylhexoic acid synthesised from ethyl malonate (Raper, T., 1907, **91**, 1837).

Action of Alkali Metals and Alkali Hydroxides on n-*Butyl Alcohol.*

The similarity of the above α-ethylhexyl alcohol and that (b. p. 181°) obtained by Guerbet from butyl alcohol led to the investigation of the action of sodium and sodium hydroxide on *n*-butyl alcohol.

Guerbet (*loc. cit.*) deduced his formula from the results of an analysis of the mixture of acids formed by the oxidation of the alcohol by means of a chromic acid mixture, and it was considered necessary to repeat his work.

The method adopted in all experiments was to dissolve the sodium in the butyl alcohol and heat the solution of sodium butoxide in butyl alcohol in a silver beaker in an electrically heated autoclave

at various temperatures and for varying lengths of time. The hydrogen was allowed to escape from a valve, the pressure in the autoclave being kept at 40—50 atmospheres.

After cooling, the product was treated with water, and the alcoholic layer separated and washed with water. The combined aqueous portions were saturated with common salt, and the alcohol separating was added to the main bulk.

After distillation in a current of steam to remove all alcohol, the aqueous part was acidified with sulphuric acid, the liberated acids were collected, and the aqueous layer was distilled in a current of steam to recover all acid.

The alcohol was dried by means of common salt, the water being separated as brine, and the acid with calcium chloride.

Typical results are given in the following table, 500 grams of *n*-butyl alcohol being used in each experiment.

Sodium. Per cent.	Conditions.	Hydrogen evolved. Litres.	Octyl alcohol. Grams.	*n*-Butyric acid. Grams.	Octoic acid. Grams.
5	To 275° and cooled	37·0	107	98	7
10	To 225° „ „	45·6	124	157	6
10	200° for 20 hours	—	216	199	20
10	250° „ 10 „	—	212	214	21
10	To 275° and cooled	88·2	206	201	28

When 15 per cent. of sodium was employed, practically the whole of the butyl alcohol was converted into *n*-butyric and octoic acids. In one case, nearly 300 grams of octoic acid were obtained.

These experiments show that the effect of an amount of sodium up to 10 per cent. has no effect on the relative quantities of octyl alcohol and butyric acid calculated on the weight of sodium used. Above 10 per cent., the amount of acid is increased at the expense of the octyl alcohol, octoic acid being formed.

The temperature at which the reaction is carried out is unimportant so long as the heating is sufficiently prolonged.

Calcium also brings about the condensation of butyl alcohol to octyl alcohol, but very little acid is formed; thus, when 100 grams of *n*-butyl alcohol were heated with 20 grams of calcium for ten hours at 235°, 20 grams of octyl alcohol and 4·6 grams of *n*-butyric acid were obtained.

The octoic acid (Found: C=66·71; H=11·04. Calc.: C=66·60; H=11·20 per cent.) and octyl alcohol (Found: C=73·79; H=13·49. Calc.: C=73·76; H=13·94 per cent.) have boiling points (225° and 181° respectively) almost identical with α-ethylhexoic acid and α-ethylhexyl alcohol, and since the acid is formed from the alcohol by simple oxidation, it must have a corresponding constitution. Its identity with α-ethylhexoic acid was proved

by the fact that mixtures of the amide with the amide of α-ethylhexoic acid (prepared as above and by Raper's method) melted at the same temperature as the latter, namely, 101·5°.

Octylene.—α-Ethylhexyl alcohol, when passed over aluminium oxide at 380—400°, loses water, giving an *octylene*. One hundred grams of the alcohol gave 71 grams of oil and 20 grams of water. The oil was fractionated as follows:

Up to 110°	9 grams.
110—125	53 „
Above 125	8 „

The pure octylene boils at 121°.

Dioctylene.—When the octylene is shaken with 80 per cent. sulphuric acid, a pleasant-smelling oil is formed, which boils at 245—250°. It is a hydrocarbon of the empirical formula C_8H_{14}, probably a *dioctylene*.

Fifty grams of the octylene, when shaken with 50 grams of sulphuric acid and 10 grams of water, gave, after washing with potassium carbonate:

Up to 120°	4·5 grams.
120—220	5 „
220—260	25 „
Above 260	5·5 „

Action of Sodium Hydroxide on n-*Butyl Alcohol.*

The reaction was carried out as in the preparation of α-ethylhexyl alcohol, sodium hydroxide being used in place of metallic sodium.

Typical experiments are given in the following table:

Sodium hydroxide. Grams.	*n*-Butyl alcohol. Grams.	*n*-Butyric acid. Grams.	α-Ethylhexoic acid. Grams.
150	500	233	5
250	760	414	10
400	760	700	25

The mixture was in each case heated at 275° for about three hours, the heating being stopped when no more hydrogen was evolved. In all cases, the unchanged alcohol was recovered, the loss varying from 1 to 5 per cent. of the whole. The method of working up was the same as that employed in the preparation of α-ethylhexyl alcohol. In addition to the production of *n*-butyric and α-ethylhexoic acids, about 1 per cent. of α-ethylhexyl alcohol was formed.

Action of Calcium Oxide and Hydroxide on n*-Butyl Alcohol.*

The amount of acid produced from *n*-butyl alcohol by the action of calcium is much less than that formed by sodium, and this fact leads to the conclusion that calcium hydroxide is much less active in the production of acid than sodium hydroxide.

Two experiments carried out with calcium oxide and hydroxide confirmed this.

Calcium Oxide.—One hundred grams of *n*-butyl alcohol and 40 grams of quicklime, when heated for eleven hours at 250—260°, gave, during the first hour, 800 c.c. of hydrogen, during the second hour 300 c.c., and after that none.

The products consisted of 6·5 grams of *n*-butyric acid and 14 grams of α-ethylhexyl alcohol, which on redistillation gave 12 grams of alcohol boiling at 180—185°. The yield of *n*-butyric acid was only 25 per cent. on the *n*-butyl alcohol attacked by the quicklime.

Calcium Hydroxide.—After ten hours' heating at 250—260°, 100 grams of *n*-butyl alcohol and 40 grams of slaked lime gave only 100 c.c. of hydrogen, 0·6 gram of *n*-butyric acid, and 1 gram of α-ethylhexyl alcohol.

Acetic Acid from Ethyl Alcohol.

Owing to the ease with which *n*-butyric acid can be obtained from *n*-butyl alcohol by heating with sodium hydroxide, an attempt was made to apply the reaction to the production of acetic acid from ethyl alcohol. Two preliminary experiments only were carried out, but these showed that the process could not be a commercial success.

Expt. 1.—Fifty grams of ethyl alcohol and 20 grams of sodium hydroxide were heated at 230—250° for three and a-half hours, the product being dissolved in water, acidified with sulphuric acid, and distilled to dryness under diminished pressure.

The acetic acid in the distillate, estimated volumetrically, was 4 grams, or 13 per cent. on the sodium hydroxide.

Expt. 2.—Sixty grams of ethyl alcohol and 20 grams of sodium hydroxide were heated for seventeen and a-half hours at 250—260°. The product was worked up as above, and 8 grams of acetic acid were obtained, that is, 26 per cent. on the sodium hydroxide.

Not only was the yield of acetic acid poor, but much of the alcohol was not recovered, owing to the formation of much resin. From this it seems probable that either acetaldehyde or a substance which readily gives this is formed as an intermediate product.

n-*Hexyl Alcohol and* n-*Hexoic Acid.*

The experiments on the production of hexyl alcohol and hexoic acid from a mixture of *n*-butyl and ethyl alcohols were not very successful, the yields being very poor.

The three following experiments may be quoted as typical of those carried out.

Expt. 1.—A solution of 50 grams of sodium in 250 grams of *n*-butyl alcohol and 200 grams of ethyl alcohol was heated in the autoclave to 275°, and then allowed to cool. The product was dissolved in water, the alcohols distilled in a current of steam, and salted out from the distillate by means of potassium carbonate. The acids were liberated from the aqueous portion by means of sulphuric acid, separated, dried, and distilled, acetic acid remaining in the aqueous portion. On redistillation, 45 grams of an acid boiling at 198—202° were obtained.

Expt. 2.—Seventy-five grams of sodium were dissolved in ethyl alcohol, and the excess of the latter was evaporated under diminished pressure. The sodium ethoxide was dissolved in 500 grams of *n*-butyl alcohol, and the solution treated as before, 75 grams of an acid boiling at 198—202° being obtained.

Expt. 3.—A solution of 70 grams of sodium in 450 grams of *n*-butyl alcohol and 140 grams of ethyl alcohol was heated at 275° and treated as in Expt. 1. From this, 82 grams of an acid boiling at 198—202° were obtained, and from the alcohol boiling at above 125°, in addition to α-ethylhexyl alcohol (b. p. 181°), an alcohol boiling at 166—168° was isolated. The corresponding acid, when purified, boiled at 199—200° and melted at 3°.

The amide melted at 97—98°, and a mixture of this with the amide of *n*-hexoic acid melted at 98—99°. The acid is therefore *n*-hexoic acid and the alcohol is *n*-hexyl alcohol.

Δ^{γ}-*Heptylene-β-one* (n-*Butylideneacetone*).

n-Butaldehyde and acetone in molecular proportions are shaken with 1—2 per cent. of solid sodium hydroxide; after a few minutes, the mixture emulsifies and becomes almost solid and very hot. The yield is not increased by cooling, but the amount of material of high boiling point is decreased. The temperature rises to 50—60°, and when it begins to fall the reaction is complete. The mixture is pale yellow, and, on cooling, water separates and the mixture becomes cloudy.

On distillation, in addition to butylideneacetone and unchanged materials, a small quantity of hydrocarbons (b. p. below 120°) is

obtained, presumably formed by the dehydration of butylideneacetone. The same hydrocarbons are apparently obtained by the action of aluminium oxide on a mixture of butaldehyde and acetone (see below).

The results of experiments with 65 grams of *n*-butaldehyde, 50 grams of acetone, and 2 grams of sodium hydroxide are as follows:

Conditions.	Up to 140°. Unchanged. Grams.	140—180°. Butylideneacetone. Grams.	Above 180°. Tar. Grams.
Shaken for 12 hours at 37° ...	22·0	30·0	27·0
,, ,, 12 ,, 15° ...	22·0	22·0	24·5
Shaken for 12 hours	19·0	18·0	34·0
Shaken in the cold	31·5	36·0	18·0
Shaken without cooling	28·0	34·5	23·0

The loss in all cases is due to acetone dissolved in the washing with water, so that the method of working up without allowing to remain gives not only a higher yield of butylideneacetone, but also less material of high boiling point, which may be regarded as loss.

No indication of mesityl oxide or phorone was obtained in the material of high boiling point. From the fraction 165—220°, α-ethyl-Δ^{α}-hexenealdehyde was isolated in appreciable quantities, but the main constituent of this fraction was butylideneacetone.

Δ^{γ}-*Heptylene-β-one* (n-*butylideneacetone*) is a colourless liquid which rapidly turns yellow on exposure to the air. The pure ketone boils at 157°, but on distillation always leaves some residue, which suggests that auto-condensation takes place, or that the compound absorbs water from the air, giving the "aldol," which decomposes to some extent on distillation, and is also readily oxidised by the air.

Ultimate analysis gives low results (compare Franke and Kohn, *Monatsh.*, 1899, **20**, 876, who found the same in the case of *iso*butylideneacetone). After very careful drying, treating with calcium chloride for two weeks, and distilling in a vacuum, the following result was obtained:

0·1102 gave 0·2957 CO_2 and 0·1007 H_2O. C=73·18; H=10·22.

$C_7H_{12}O$ requires C=74·93; H=10·79 per cent.

The *semicarbazone*, $C_8H_{15}ON_3$, is readily soluble in alcohol and melts at 118°.

On dehydration with 60 per cent. sulphuric acid (Kipping and Perkin, T., 1890, **57**, 13) or on heating with sodium hydrogen sulphate at 150°, butylideneacetone gives an oil with a terpene-like odour and much tar.

Action of Reduced Copper.—By passing butylideneacetone over

carefully reduced copper oxide heated to 700—800°, a small quantity of toluene was obtained, together with some phenolic substance, which appears to be a cresol, probably formed in the following manner:

$$\begin{matrix}Me\\O\end{matrix}\!\!>\!C\!\diagup\!\begin{matrix}CH{=}CH\\CH_3{\cdot}CH_2\end{matrix}\!\!>\!CH_2 \rightarrow \begin{matrix}Me\\HO\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH{=}CH\\CH_2{\cdot}CH_2\end{matrix}\!\!>\!CH_2.$$

This compound then loses four atoms of hydrogen, and the hydroxyl group migrates, giving a cresol. Most of the butylideneacetone, however, is converted into carbon and gaseous products. Experiments were carried out at various temperatures, but whenever toluene was obtained, the greater part of the ketone gave carbon and gases. At 600° a 5 per cent. yield of toluene was obtained.

Action of Aluminium Oxide on a Mixture of n-*Butaldehyde and Acetone.*

By passing butylideneacetone over aluminium oxide at 300°, it loses water, giving unsaturated hydrocarbons, which are apparently the same as those obtained in the preparation of the ketone by means of solid sodium hydroxide.

This led to the investigation of the action of aluminium oxide on a mixture of *n*-butaldehyde and acetone.

When a mixture of molecular proportions of *n*-butaldehyde and acetone is passed over aluminium oxide at 300—350°, water is lost and a certain amount of butylideneacetone is formed. This, however, seems to be an intermediate product, which on further dehydration gives two hydrocarbons, C_7H_{10}, possibly of the formulæ $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}C{:}C{:}CH_2$ and

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}C{:}CH.$$

One of these appears to boil at about 100°, and gives a precipitate with ammoniacal cuprous chloride. It is therefore an acetylenic hydrocarbon. The other boils at about 60—70°.

Only a few preliminary experiments have been made, but the optimum temperature appears to be about 325—350°. Above 400° charring takes place on the aluminium oxide, but at 350° the catalyst will apparently dehydrate an unlimited amount of butaldehyde and acetone.

Butylideneacetone only has been definitely proved to be present in the product.

The experiments which have been carried out with 50 grams of *n*-butaldehyde and 40 grams of acetone can be summarised as follows:

	i. Grams.	ii. Grams.	iii. Grams.
Oil	62·0	71	74
Water	16·5	13	9

Fractionation of the oil gave:

Up to 100°	24·0	38	41·5
100—125	2·0	3	4·0
125—145	2·5	3	4·5
145—170	18·0	12	12·0
170—200	3·0	3	3·0
Above 200	6·5	8	5·5

In this series of experiments, the more rapidly the materials were passed over the catalyst, the less water was produced and the more butylideneacetone (145—170°). This points definitely to the latter being an intermediate product in the formation of the hydrocarbons of low boiling point, and this is borne out by the results obtained on passing butylideneacetone over aluminium oxide, when water is lost. Thus, 42 grams of butylideneacetone yielded 32 grams of oil which, on fractionation, gave:

Up to 65°	1·0 gram.
65—140	5·5 grams.
140—170	18·0 „
Above 170	7·0 „

Action of Aluminium Oxide on a Mixture of n-*Butyl alcohol and Acetone.*

A mixture of 460 grams of acetone and 590 grams of *n*-butyl alcohol was passed over aluminium oxide at 300—350°.

The product consisted of 550 grams of oil and 238 grams of water, and much gas was evolved. Fractionation of the oil gave:

	Grams.		Grams.
Up to 55°	30	115—125°	73
55— 65	126	125—145	6
65— 75	24	145—155	48
75— 85	22	155—180	6
85— 95	18	180—210	35
95—105	21	Above 210	53
105—115	61		

From this the following products have been isolated:

(i) A *hydrocarbon*, boiling at 76—78°, probably C_7H_{14} from (iv) by dehydration.

(ii) A *heptadiene*, boiling at 94—96°:

0·1273 gave 0·4088 CO_2 and 0·1538 H_2O. C=87·57; H=13·51.
C_7H_{12} requires C=87·41; H=12·59 per cent.

This is probably formed by the dehydration of methyl amyl ketone (iii).

(iii) Methyl amyl ketone (b. p. 148—150°), which was isolated by means of its sodium hydrogen sulphite compound. The melting point of its semicarbazone (120°) was not altered by admixture with a specimen from another source.

(iv) An unsaturated *alcohol*, boiling at 150°, probably isomeric with methyl amyl ketone.

Substances boiling at 70—80°/13 mm. and 100—110°/13 mm., together with traces of *n*-butaldehyde and *iso*propyl alcohol, were also isolated.

The chief products were methyl amyl ketone and the heptadiene.

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XLII.—*An Investigation of the Resin from Species of Xanthorrhoea not previously examined.*

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XANTHORRHŒA resin has been the subject of many investigations, but unfortunately the authors of these investigations do not always seem to have been certain as to the species from which the resin had been derived. For the most part, the resin examined appears to have been obtained from New South Wales, and is described as "red" or "yellow." Tschirch in his "Harze und Harzbehälter" says: "Was die Abstammung der Acaroide betrifft, so ist dieselbe noch nicht sichergestellt. Für das gelbe wird *X. hastilis*, für das rothe meist *X. australis* angegeben." In the most recent examination made at the Imperial Institute, no reference is made to species, but the material used is described as "a commercial sample of red Xanthorrhœa resin."

The two species above referred to are not known in South Australia, and all the material used by us was obtained either from Kangaroo Island (South Australia) or West Australia. So far as the Kangaroo Island resin is concerned, we have again red and yellow varieties. The yellow has, so far as can be gathered from specimens of foliage, been obtained from *X. Tateana*, but, according to Mr. Harrison, of Kingscote, only about 1 per cent. of the trees yield the yellow resin. The origin of the red is still

uncertain. A specimen of foliage was submitted to Prof. Osborn of this University, who states that it would require investigation by a specialist on the spot to determine whether the leaves belong to a different species (from that which yields the yellow), or a variety, or whether age and environment may account for the differences in the leaves.

Those chemists who have published results of their work on the "red" and "yellow" resins agree substantially as to the products so far obtained, but some have found substances not noticed by others. As our work is concerned with material from species not, so far as we are aware, yet examined, it will suffice merely to mention the principal constituents recorded in resins from other species. Those are, briefly:

(1) *Acids*, either free or partly in the form of *esters*.—Benzoic, cinnamic, *p*-coumaric.

(2) *Aldehydes*.—Vanillin, *p*-hydroxybenzaldehyde.

(3) *Products of Oxidation by Alkaline Permanganate, Chromic Acid, etc.*—Acetic and oxalic acids, or insoluble chromium compounds.

(4) *Products of Fusion with Potassium Hydroxide*.—Resorcinol, *p*-hydroxybenzoic acid, carbonic acid.

(5) *Products of Action of Nitric Acid*.—Picric acid, *p*-nitrophenol, acetic acid.

(6) *Products of Distillation with Zinc Dust in the Presence of Hydrogen*.—Benzene, toluene, naphthalene.

(7) *Products of Destructive Distillation*.—Phenol, styrene, and tarry matters.

(8) A residue obtained by acidification of an alkaline solution consisting of a complex substance, which has been named a "resinotannol."

A. *Examination of the "Red" Resin.*

The resin used in the following experiments was carefully picked out and freed, as far as possible, from fragments of leaves, the quantity of which was quite insignificant.

Action of Nitric Acid.

Picric acid was obtained in quantity, and small quantities of another nitro-compound, which was not identified. Oxalic acid was also obtained.

Fusion with Sodium Hydroxide and Examination of the Product for Volatile Acids.

About 500 grams of the resin in 50-gram lots were fused gently for several hours with an equal weight of sodium hydroxide, a little water having been added. The fusion was acidified with sulphuric acid, distilled, and the distillate neutralised with sodium carbonate and evaporated to dryness. The greater part of the residue was added to a cold mixture of alcohol and concentrated sulphuric acid, frequently shaken, and allowed to remain overnight. The liquid was then gently distilled, and the distillate shaken several times with a saturated aqueous solution of potassium carbonate, the layer of ester run off, dried with potassium carbonate, and fractionated. The greater part of the distillate (apart from ether, due to the interaction of the alcohol and sulphuric acid) was found to be ethyl acetate, but there was also present a small fraction which had an odour like that of ethyl butyrate, and, on hydrolysis and acidification, gave the unmistakable odour of butyric acid. The total yield of esters was about 8 per cent. of the resin taken.

Oxidation with Alkaline Permanganate.

Twenty grams of the resin were boiled with alkaline permanganate (10 grams of $KMnO_4$ in 200 c.c. of solution) for half an hour, the solution then being acidified with sulphuric acid and distilled in a current of steam. Only traces of acid (acetic?) were present, with a minute quantity of a fragrant oil. The residue from the steam distillation was collected, washed, redissolved in sodium hydroxide solution, a further 10 grams of potassium permanganate added, and distilled. The distillate was neutral. On repeating the process, the resin was ultimately broken up, and nothing but carbonic acid could be recognised in the final product.

Examination for Acids either Present in the Free State or in the Form of Esters.

A large quantity of the resin (680 grams) was dissolved by the aid of excess of sodium hydroxide in about 2 litres of water, and the solution distilled in a current of steam for about twelve hours. The residue was just acidified with sulphuric acid, the solution filtered, and concentrated until a quantity of sodium sulphate crystallised out, the crystals (which were mixed with a crystalline organic substance) were warmed with alcohol, the latter was distilled off, and the tarry residue, as well as the acid solution, ex-

hausted with ether. The residue, after distillation of the ether, partly solidified on keeping, but contained some tarry matter, which, after considerable difficulty, was removed by exhaustion with boiling water and repeated treatment with animal charcoal. Ultimately, a nearly colourless, crystalline mass was obtained, and this was separated by means of chloroform into two substances, which, on examination, proved to be *p*-coumaric acid and *p*-hydroxybenzaldehyde. It seems scarcely necessary to go into details of the identification of these substances, repeatedly recognised as they have been by others as present in other varieties of Xanthorrhœa resin; suffice it to say that the former was fully identified by combustion, melting point, and other characteristics, the latter by methylation, conversion into anisaldehyde, and oxidation of the latter to anisic acid. The total yield of the two products (purified) was about 4·5 per cent., but it must be noted (a fact of which we were not at the time aware) that *p*-coumaric acid is slowly decomposed on boiling with dilute sulphuric acid. Hence the amount of this acid obtained in the way described above is no doubt considerably below that actually present. It was not thought necessary to make a careful search for other acids or aldehydes such as benzoic and cinnamic acids and vanillin, which have been found by other observers, but it is worth mentioning that, on acidification of the alkaline solution of the resin after steam distillation, for the purpose of extraction of the above-mentioned substances, a vanillin-like odour was often noticed.

Products obtained by Steam Distillation of a Strongly Alkaline Solution.

In the experiment above described, it was noticed that an appreciable quantity of a fragrant oil was obtained in the distillate. On shaking the distillate (6 litres) with ether and evaporating off the latter, about 1·5 grams of a fragrant oil remained, which, on keeping, solidified to a pale brown, crystalline solid. In order to examine this more thoroughly, several lots, of 1 kilogram each of the resin, were dissolved in alkali (about 200 grams of sodium hydroxide and 2 litres of water to each kilogram), and steam distillation was continued in each case until about 12 litres of distillate were collected and practically no more oil passed over. The distillates were then exhausted with benzene and the latter distilled off. From each such distillation, from 3·55 to 3·65 grams of residual oil were obtained, which, on keeping, always solidified. The total amount of material was then dissolved in alcohol, the solution filtered from a minute amount of insoluble matter, and

the material allowed to crystallise. Two recrystallisations brought the melting point to 49°, at which point it remained constant. The crystals were stout, well-developed needles, almost colourless, and had a sweet odour. (This fragrance was subsequently found to be due to a minute quantity of a fragrant oil, which was not present in sufficient quantity for identification, and adhered persistently. The crystals, when afterwards thoroughly purified, were found to have only a slight, somewhat phenolic odour.) They were freely soluble in ether, benzene, acetic acid, and most other organic solvents, very sparingly so in cold water, more freely in hot, readily soluble in solutions of alkali hydroxides, but insoluble in solutions of the alkaline carbonates or ammonia (Found: C=64·78, 64·71; H=5·99, 5·78. M.W. by cryoscopic method in benzene, 161. $C_9H_{10}O_3$ requires C=65·06; H=6·02 per cent. M.W.=166).

On treatment with bromine in carbon tetrachloride solution, it yielded a crystalline bromo-derivative, and on acetylation an acetyl derivative melting at 44—45°. The hydrazone was also obtained. These facts agree with the data for paeonol, a product obtained from *Paeonia Moutan* in Japan, and used medicinally in that country. Its constitution has been proved to be that of 2-hydroxy-4-methoxyacetophenone, $CH_3\cdot CO\cdot C_6H_3(OH)\cdot OMe$ (Nagai, *Ber.*, 1891, **24**, 2847; Tahara, *ibid.*, 2459).

The mother liquor, after separation of the paeonol, contained apparently nothing but a small quantity of the fragrant oil already referred to, the quantity of which was too small for examination.

Nitropaeonol.

For reasons which will appear in the sequel, it became desirable to prepare a nitropaeonol. Ten grams of paeonol in 30 c.c. of glacial acetic acid were mixed with 5 c.c. of nitric acid (D 1·41). After a few minutes, a characteristic, blue colour appeared, changing in the course of some hours to blood-red. For twelve hours after no further change took place, but on adding a further 10 c.c. of nitric acid, the mixture became warm, and, after a few minutes, deposited a crop of crystals, nitrous fumes being evolved in quantity and the red colour persisting. After remaining for some days, the liquid was diluted with its own volume of water, the crystalline deposit collected, washed, and repeatedly crystallised from hot alcohol until almost colourless. It consisted of long, straw-coloured needles melting at 153° (Adams, *J. Amer. Chem. Soc.*, 1919, **41**, 247, gives 155°) (Found: N=6·56. $C_9H_9O_5N$ requires N=6·63 per cent.). On reduction with tin and hydrochloric acid, removal of the tin by means of hydrogen sulphide, and concentration of the

filtered solution, the hydrochloride of the amino-compound separated out as a mass of needles, which were permanent in air but were not further examined.

B. *Examination of Yellow Resin of* X. Tateana. *Isolation of a New Substance*, $C_9H_{10}O_4$.

The yellow resin differs in other respects than in its colour from the red variety. It shows a marked tendency to accumulate in lumps and tears varying in colour from pale amber to a muddy brown, but it is always pure yellow when powdered. It is noticeably less brittle than the red, becomes soft if placed in the mouth, and when boiled with water becomes a mobile liquid. It dissolves in alkali hydroxides, yielding in moderate concentrations an orange solution, from which acids precipitate the resin as a dull, mustard-coloured powder. Steam distillation was resorted to under conditions exactly similar to those already described in the case of the red material, with the exception that the distillation was much more prolonged, being continued in some cases until 150 to 160 litres of distillate had been collected, the reason being that appreciable quantities of oily matter continued to pass over for long periods of time. The oil obtained in this way gradually solidified on keeping. That in the earlier part of the distillation was very like paeonol, but later on quantities of solid matter quite different from paeonol made their appearance. The whole of these substances was extracted from the distillate by shaking with benzene. The total product after the evaporation of the benzene averaged, in several distillations, about 5 per cent. of the weight of material, a very much larger quantity than in the case of the red resin. Obviously there were two substances here present, which could be partly separated by collecting separately the earlier and later portions of the distillate. The earlier portions consisted practically entirely of paeonol, with a small quantity of the same fragrant oil noted in the case of the red resin. The later portions were recrystallised from dilute alcohol until a constant melting point, 79°, was reached. In subsequent experiments, the whole of both substances was extracted with benzene, and, after removal of the latter, the two were separated by fractional distillation under 20 mm. pressure. At this pressure, the paeonol boiled at 158° and the other substance at 185°. Of the total, about 60 per cent. was paeonol, and the remainder, except for a trace of some material of higher boiling point, the second substance. The substance obtained in this way was quite colourless, practically insoluble in cold or hot water, and readily soluble in alkali hydroxides or in

the ordinary organic solvents. Like paeonol, it gives a claret colour with ferric chloride. The colour reactions with nitric acid are very similar to those given by paeonol, but more marked. In cold concentrated nitric acid, an intense blue colour is immediately developed, which, on keeping, and particularly on warming, changes to a blood-red, which is not discharged by continued boiling with concentrated nitric acid. On diluting the red solution and rendering alkaline with sodium hydroxide, a dark green colour is developed, which, however, is somewhat fugitive.

Found: C=59·47, 59·78; H=5·70; 5·23.

$C_9H_{10}O_4$ requires C=59·34; H=5·49 per cent.

A molecular-weight determination by the cryoscopic method in benzene gave 178, the theory for $C_9H_{10}O_4$ being 182.

Oxidation.—The above figures, coupled with the general behaviour of the substance, in particular the close resemblance of its colour reactions to those of paeonol, suggested the probability that we were here dealing with an hydroxypaeonol. To decide this point, the following experiments were undertaken. A small quantity, 0·532 gram, was boiled in a small flask attached to a reflux condenser with a mixture of potassium chromate and 15 per cent. sulphuric acid, the former being added cautiously until the solution was permanently yellow. The mixture was then distilled almost to dryness, water added, and the boiling resumed until acid ceased to pass over. The distillate was redistilled, excess of barium carbonate added, the solution evaporated to dryness, the residue redissolved, and the solution filtered and finally evaporated to dryness in a tared platinum dish. The barium salt so obtained, after drying at 100°, weighed 0·2979 gram, and its reactions were those of barium acetate (0·23 gave 0·206 $BaSO_4$, whilst barium acetate requires $BaSO_4$=0·21). An hydroxypaeonol on oxidation should yield acetic acid.

Oxime.—To a solution of 4 grams of sodium hydroxide in 8 c.c. of water was added slowly, with cooling, a solution of 6 grams of the original substance and 2·5 grams of hydroxylamine hydrochloride in a mixture of 80 c.c. of alcohol and 20 c.c. of ether. After remaining for twelve hours, the red solution was heated under reflux for two to three hours, the excess of alcohol and ether distilled off, and the residue poured into water and acidified. The crude oxime was repeatedly crystallised from dilute alcohol until a constant melting point was obtained. The purified compound crystallised from alcohol in transparent plates, and from the dilute solvent as a grey sand. The air-dried substance, when slowly heated, sintered together at 100° and melted and decomposed at 107°, but this was found to contain water, the loss at 100° amount-

ing to 8·44 per cent. (theory for $1H_2O = 8·37$ per cent.). Apparently hydrolysis takes place on drying, with loss of hydroxylamine, estimations of nitrogen always giving low results. There could be no doubt, however, as to the oximic character of the compound, for the original substance could readily be obtained by hydrolysis, hydroxylamine being easily recognised in the solution.

Methylation to a Dimethyl Ether.—Six grams of methyl sulphate were added to a warm paste of 5 grams of the compound $C_9H_{10}O_4$, 4 grams of sodium hydroxide, and 10 c.c. of water. The mixture became very hot, and was allowed to remain for twelve hours. The mass was then dissolved in the least possible quantity of alcohol, and the solution poured into an excess of sodium hydroxide solution. The precipitated ether was collected, washed, and recrystallised three times from dilute alcohol, when the melting point became constant at 102—103° (Tutin and Caton, T., 1910, **97**, 2067, give 99—100° as the melting point of 2 : 4 : 6-trimethoxyacetophenone). The ether so obtained was insoluble in alkali, and gave no coloration with ferric chloride. A blue colour with nitric acid developed very slowly (Found: C = 62·44, 62·35; H = 6·69, 6·60. M.W. = 205. $C_{11}H_{14}O_4$ requires C = 62·85; H = 6·65 per cent. M.W. = 210). These figures prove the existence of two hydroxyl groups in the compound $C_9H_{10}O_4$. On fusion with potassium hydroxide, a little water at temperatures ranging from 120° to 230°, acidification of the product, and repeated extraction with ether, a crystalline substance was obtained which, after purification, was completely identified by its sweet taste, bluish-violet colour with ferric chloride, colour reaction with pine wood moistened with hydrochloric acid, and analysis as phloroglucinol.

The above experiments conclusively prove that the substance, $C_9H_{10}O_4$, is a monomethyl ether of 2 : 4 : 6-trihydroxyacetophenone. The position of the methoxy-group remains to be determined. The close association of this compound with paeonol, and the similarity of its reactions to those of paeonol, render it probable that the methoxy-group is in the para-position, but so far we have been unsuccessful in definitely proving this point. It was thought possible that nitration of paeonol, reduction of the nitro- to the amino-compound, diazotisation, and decomposition by water might yield an hydroxypaeonol which would be either identical with or different from the compound under consideration. The nitration and reduction of the nitro-compound have already been described. On diazotisation of the latter, however, and boiling with water, coupling or some other change apparently takes place, and a deep brown substance is obtained, which has not been further examined.

Examination for Acids, Free or Combined.

The alkaline solution, after steam distillation, was acidified and examined exactly as described in the case of the red resin, and again *p*-coumaric acid and *p*-hydroxybenzaldehyde were identified in considerable quantity.

C. *Examination of* X. Preissii.

We are indebted to Mr. Lane-Poole, Conservator of Forests in W. Australia, for a supply of this resin, which we have examined by the same method of steam distillation, as already described. Since the work was completed, a letter was received from the Government Chemical Laboratory, W.A., enclosing a report from Mr. D. A. Herebert, the economic botanist and pathologist, in which it is stated that a new species of *Xanthorrhoea* has been discovered which is very like *Preissii*, the resin of which, however, is black, that of *Preissii* being red. The samples of resin forwarded to us by Mr. Lane-Poole were all red, however, and there was no evidence of the presence of any of the black variety. A small quantity of the black variety may have been present and escaped notice, but not sufficient, we think, appreciably to vitiate the results of our work.

Products of Steam Distillation.

On distillation with steam in the way already described, a yellow oil was obtained much more fragrant than that produced from the other species above referred to, the total yield being a little more than 1 per cent. The first portions of oil passed over very rapidly, but even after long and tedious distillation (160 litres of distillate from 3 kilograms) the distillate was still turbid. This is in sharp contrast with the result obtained with *X. Tateana*, the distillate in the latter case being quite clear when the distillation was stopped. As in previous cases, the distillate was exhausted by shaking with benzene, and the latter distilled off. The residue was then carefully fractionated under 20 mm. pressure, and ultimately five fractions were collected, namely, 110—155°, 155—165°, 165—185°, 185—200°, and 200—210°, leaving a small quantity of a somewhat viscous, uncrystallisable material in the flask. Fraction 2 (155—165°) proved to be almost entirely paeonol. Fraction 3 was chiefly paeonol with a small quantity of an oil which did not crystallise. Fraction 4 remained liquid for some weeks, but

finally deposited crystals which, on washing with small quantities of alcohol and recrystallisation, melted at 79°, and proved to be the hydroxypaeonol already described.

Isolation of a Compound, $C_{13}H_{12}O_2$.

Fraction 5 was solid, and was recrystallised from alcohol until the melting point was constant at 69·5°.

Found: C=78·24; H=6·44.

$C_{13}H_{12}O_2$ requires C=78·00; H=6·00 per cent.

The figures agree better with the formula $C_{13}H_{12}O_2$ than with $C_{13}H_{14}O_2$.

A molecular-weight determination by the cryoscopic method in benzene gave 194 ($C_{13}H_{12}O_2$ requires 200). The substance is practically insoluble in cold or hot water and in alkali hydroxides, but dissolved easily in the ordinary organic solvents. Its alcoholic solution gives no coloration with ferric chloride. It is not acted on by acetic anhydride. All attempts to form from it an oxime or hydrazone failed. On the other hand, it was found to contain one methoxy-group, an estimation by the ordinary method giving OMe=15·1, whilst $C_{12}H_9O{\cdot}OMe$ requires OMe=15·5 per cent. With cold concentrated nitric acid, a black, tarry material was at once formed, with evolution of nitrous fumes, but on slow evaporation an orange substance remained, from which nothing definite has so far been obtained. Potassium dichromate and dilute sulphuric acid attack it very slowly, and again no definite product could be obtained. It dissolved gradually in cold concentrated sulphuric acid, forming a pale yellow solution, from which, on dilution, it was deposited apparently unchanged. With hot concentrated sulphuric acid, dirty green solutions were obtained, which at the fuming point assumed a rich purple tint, but no charring took place, and the solution, on pouring into water, yielded a flocculent, red precipitate. These facts appear to indicate that the compound is a methoxydiphenyl ether, and its general characters are in harmony with that supposition. Derivatives of diphenyl ether, with few exceptions, appear to have been little studied, and all seem to be characterised by considerable stability.

An attempt was made to synthesise *p*-methoxydiphenyl ether by the preparation of *p*-nitrodiphenyl ether, its reduction to the amino-compound, the diazotisation of the latter, the decomposition of the diazo-compound with water, and methylation of the product. The first stage was carried out successively by Haeussermann and Teichmann's method (*Ber.*, 1896, **29**, 1446). A mixture of

potassium phenoxide, excess of phenol, and *p*-chloronitrobenzene was heated for two to three hours in an oil-bath to 150—190° in a flask with reflux condenser, a stream of hydrogen being passed through the apparatus. On cooling the mass, water was added, and the alkaline solution extracted with ether. The residue, after evaporation of the latter, was distilled under 20 mm. pressure, and practically pure *p*-nitrodiphenyl ether obtained. The reduction of the nitro-compound was effected without difficulty, and the amino-compound obtained in white crystals. On diazotisation and boiling with water, a tarry mass was produced, which was extracted with ether, and the residue, on evaporation of the latter, methylated by methyl sulphate in alkaline solution. The material which separated was small in quantity, and on distillation yielded only a small quantity of liquid boiling at 170°/20 mm., which was not the desired compound. We hope to make further experiments in the future.

Isolation of Citronellol.

Fraction 1 (110—155°) of the oil from *X. Preissii* was carefully fractionated, with the result that a large proportion of it was obtained as a fragrant oil boiling at 118—120°/20 mm. with smaller quantities of fragrant substances of lower boiling point. It was colourless, somewhat viscid, and had a distinct rose-like odour, quite different from that of geraniol, which it was at first suspected to be. To ascertain whether any esters were present, the ester value was determined by boiling with alcoholic potassium hydroxide and titrating with sulphuric acid, but was found to be only 14. On acetylation, however, the ester value rose to 280, which corresponds with 96—98 per cent. of acetates derived from the possible alcohols $C_{10}H_{16}O$, $C_{10}H_{18}O$, or $C_{10}H_{20}O$. In order further to purify the oil, it was heated under reflux with fairly concentrated alcoholic potassium hydroxide, a treatment which had no effect on the odour or boiling point (Found: C=76·56; H=13·14. $C_{10}H_{20}O$ requires C=76·92; H=12·82 per cent.).

This alcohol proved to be optically active, a solution of 2·369 grams in 20 grams of benzene giving a rotation of −1·1° at 13° in a 2-dcm. tube. Hence $[\alpha]_D^{13}$ −5·27°, which is not far from the value −4·20° ascribed to *l*-citronellol. The identity with citronellal was finally determined by conversion into the hydrogen phthalic ester. To the above solution in benzene were added 2·5 grams of finely powdered phthalic anhydride, and the mixture was boiled under reflux for five hours. The benzene having been distilled off, a viscid oil remained which, on keeping overnight, partly solidified. On washing with light petroleum, the oil was separated

from the crystals, which proved to be unchanged phthalic anhydride. From the petroleum washings the ester was recovered by distillation of the solvent as a colourless, permanent oil without odour. It was completely soluble in potassium hydroxide. On adding an almost neutral solution of the hydrogen phthalic ester in sodium carbonate to a fairly concentrated solution of silver nitrate, a white, curdy, silver salt was precipitated, which was obtained in small rosettes of very fine needles by crystallisation from boiling methyl alcohol. After drying in a vacuum, these melted at 125°, and on ignition gave Ag=25·89 (Calc.: Ag=26·23 per cent.). These facts leave no doubt as to the identity of the oil with citronellol.

It is noteworthy that the higher fractions obtained by the distillation of the crude oil had an odour of mint. This suggests the presence of *iso*pulegol, which would probably be formed during the repeated fractionation of the crude oil if it contained some citronellal, which is quite probable (compare Schimmel's *Reports*, April, 1909, p. 94).

Examination for Acids.

An examination of *X. Preissii* for acids led to the identification of *p*-coumaric acid, but *p*-hydroxybenzaldehyde was not detected, although it may have been present in small quantity.

Residues after Steam Distillation and Acidification.

The solids obtained by acidifying the alkaline solutions after steam distillation have been carefully washed and preserved. We hope soon to investigate them more thoroughly.

Summary.

(1) The *Xanthorrhoea* resins from Kangaroo Island and W. Australia, in common with other species examined by various chemists, contain *p*-coumaric acid, either in the free state or in the form of an ester, and *p*-hydroxybenzaldehyde.

(2) By steam distillation from a strongly alkaline solution, the following substances not hitherto found in Xanthorrhœa resin have been obtained:

A. *Red Resin from Kangaroo Island* (Sp. ?).—(*a*) A small quantity of fragrant liquid of vanillin-like odour; (*b*) paeonol (2-hydroxy-4-methoxyacetophenone); (*c*) traces of material of higher boiling point.

B. *Yellow Resin from* X. Tateana (*Kangaroo Island*).—(*a*) A small quantity of fragrant liquid of vanillin-like odour; (*b*) paeonal in much larger quantity than in the red resin; (*c*) hydroxypaeonol in quantity about two-thirds of that of the paeonol; (*d*) a small quantity of material of higher boiling point.

C. *Red Resin from* X. Preissii (*W. Australia*).—(*a*) A small quantity of fragrant liquid not identified; (*b*) *l*-citronellol; (*c*) paeonol; (*d*) hydroxypaeonol; (*e*) a compound, possibly methoxydiphenyl ether; (*f*) a small quantity of so far uncrystallised material of very high boiling point.

This investigation has been carried out by us as a special committee appointed for the purpose by the Australian Commonwealth Institute of Science and Industry.

We have to thank Mr. W. W. Hurst, originally a member of the Committee, for help rendered in the earlier part of the work, and Mr. F. L. Winzor for great assistance in the latter portion.

The University,
Adelaide.

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XLIII.—*Coagulation of Metal Sulphide Hydrosols. Part II. Influence of Temperature on the Rate of Coagulation of Arsenious Sulphide Hydrosols.*

By Jñanendra Nath Mukherjee.

Certain observations of Linder and Picton (T., 1905, **87**, 1906) show that temperature has a very marked and anomalous effect on the coagulating power of an electrolyte. It is similar to the irregular effect of dissolved hydrogen sulphide observed by the author and Sen (T., 1919, **115**, 462). The effect of temperature on the velocity of coagulation is undoubtedly of importance for the elucidation of the mechanism of coagulation, but, unfortunately, little has been done on the subject. In their work, Linder and Picton did not attempt any study of the effect of temperature on the rate of coagulation. Moreover, as they employed an unsound method of measuring the coagulating power, their results are inaccurate, as would appear from the following quotation: "The required concentration of the salt is generally diminished by rise of temperature. Thus, at 15° and 70°, the volume of $N/25$-calcium chloride was 3·85 and 2·30 c.c. respectively, the latter representing

a decrease of 40 per cent. Similar results were obtained with calcium nitrate, hydrochloric acid, strontium nitrate, and aluminium sulphate. On the other hand, the reverse effect was noticed with ammonium chloride, sulphuric acid, and ammonium sulphate. Thus, at 13° and 61°, the volume of $N/2$-ammonium chloride was 3·47 and 4·44 c.c. respectively, the latter representing an increase of 28 per cent." In his experiments, Paine (*Proc. Camb. Phil. Soc.*, 1912, **16**, 430) remarks: "There is no very marked change (but slight increase) in the rate of coagulation on raising the temperature to 100°." He warmed his sols to hasten the separation of what he called "the coagulated portion."

EXPERIMENTAL.

The procedure described in the former paper (*loc. cit.*) was employed. Colloidal solutions like those studied are always "ageing," and the observations should always be simultaneous. The data only show the comparative effects of the particular condition hat is changed. The method used herein is sufficiently accurate or the purpose in view, and unless the process of "ageing" has ieen fully accounted for, there is not much need to make it more ccurate. However, the method can easily be made instrumental and as accurate as desirable, and the author is at present engaged n this with a view to elucidate the stability relations of these sols.

In the case of dilute sols, the mixture of electrolyte and sol was continuously kept stirred by jerking the tube with the hand. This gives a sharp change for the first appearance of visible particles throughout the liquid. For sols rich in sulphide, this was not done, for reasons given before (*J. Amer. Chem. Soc.*, 1915, **37**, 2024), and the times for perceptible change and for certain definite degree of opacity were noted.

Five c.c. of electrolyte and 5 c.c. of sol were immersed in a beaker containing water, which was suspended inside a thermostat. About one-fourth of the length of the tubes remained above the surface of the water. In order to minimise the errors in measuring the volumes, the same two pipettes were always used, one for the sol and the other for the electrolyte, thus keeping the relative volumes constant. This is a necessary precaution to obtain trustworthy agreement between different readings. After the liquids in the tubes had attained the temperature of the bath (about an hour), they were withdrawn, and the electrolyte was added to the sol. The test-tube containing the liquid was then again immersed in the water of the beaker. The whole process does not take more than half a minute. The tubes were taken up from time to time and observed.

Different preparations of the sol were always tried, and at least two readings taken. At least four different concentrations of the same electrolyte were used. The results are concordant. The electrolytes studied were hydrochloric acid, potassium chloride, sodium chloride, lithium chloride, potassium sulphate, potassium nitrate, sulphuric acid, barium chloride, calcium chloride, calcium bromide, strontium chloride, magnesium chloride, magnesium sulphate, aluminium sulphate, and thorium nitrate. The salts were purified samples of the best materials available.

It is possible that, on heating, the sol undergoes an irreversible change. In order to test this, samples of sol and electrolyte were heated in the bath along with the others, for the same interval of time, and were then cooled and the times for the respective changes noted. There was no perceptible difference between these samples and others which were not so heated, showing that there is no irreversible change under these conditions within the limits of experimental error. It is necessary to treat the electrolyte similarly to see whether there has been any appreciable change in its concentration due to loss by evaporation. In general, the observations were finished within five hours, and in some cases within two hours, after immersing the tubes in the bath. It is interesting to note in this connexion that Kruyt and Spek (*Kolloid Zeitsch.*, 1919, **25**, 1) find that on long-continued boiling of arsenious sulphide sols at 100—105°, the size of the particles decreases markedly. In the present instance, the temperature effect must be explained in terms of a reversible change in the quality of the sol in case it undergoes any such change.

The results show an irregular effect analogous to that noticed by the author and Sen with dissolved hydrogen sulphide (*loc. cit.*). The electrolytes can be broadly classified in groups determined by their valency. Within each group the results are perfectly regular, and, so far as can be judged, the different cations in the same group are affected in an equal degree by any given variation in the conditions of experiment. Contrary to the observation of Linder and Picton quoted above, both hydrochloric acid and sulphuric acid effect a diminution in stability at higher temperatures. In this respect, the hydrogen ion behaves in a different way from the rest of the univalent cations.

With cations of the barium group there is in each case a diminution in stability with rise in temperature. The experiments with aluminium and thorium salts will be dealt with separately, because of certain striking peculiarities. In the following table, a few of the data with uni- and bi-valent cations are recorded for comparison. The times given denote the interval, after mixing the

sol and the electrolyte, necessary to produce a definite change in the sol. The concentrations refer to "end" concentrations. As stated before, the change in the sol which is observed varies with the nature of the sol. The times are strictly comparative only for a particular sample observed at different temperatures. The observations at different temperatures were made side by side and always on the same day. The sulphide contents of the different sols are given below. Sol *A* contains 1·925 millimoles of arsenious sulphide. Sols *B*, *C*, and *F* have the same sulphide content, namely, 14·23 millimoles per litre. Sols *D*, *E*, and *I* contain ·5575 millimoles of sulphide per litre, but sol *E* contains an equal mount of arsenious oxide in excess. Sols *H* and *J* each con- ain 4·8 millimoles per litre. In comparing the different sols, it hould be remembered that the behaviour of a sol is not determined y its sulphide content alone.

TABLE I.

Electrolyte.	Concentration.	Sol used.	Times required at different temperatures 25°.	45°.
1. Potassium chloride	17*N*/200	*A*.	4 mins.	38 mins.
2. " "	*N*/20	*B*	14 "	38 "
3. " "	*N*/18	*B*.	4 "	10 "
4. " nitrate	*N*/20	*C*.	1 hr. 51 mins. (14·5°)	3 hrs. 39 mins.
			14·5°.	45°.
4. Potassium sulphate	*N*/7	*D*.	3½ mins.	4 hrs. 2 mins.
5. " "	*N*/7	*E*.	1 min.	20 mins.
6. Sodium chloride...	3*N*/40	*F*.	10 mins.	4 hrs. 42 mins.
7. Hydrochloric acid	0·07385*N*	*D*.	5 "	about 1 min.
8. " "	0·07385*N*	*E*.	4 "	" 1½ mins.
9. Sulphuric acid ...	0·08438*N*	*E*.	40 "	23 mins.
10. Hydrochloric acid	0·0733*N*	*E*.	11 "	3 "
			28°	65°.
11. Barium chloride ...	*N*/800	*H*.	5 mins.	1 min.
12. Calcium bromide ...	*N*/800	*H*.	13 "	2 mins.
13. Strontium chloride	*N*/800	*H*.	21 "	4½ "
14. Magnesium sulphate	*N*/600	*H*.	7 "	2 "

Observations 1 and 2, 1 and 3, and 5 and 6 show clearly that the effect of temperature depends on the quality of the sol. The concentration of the electrolyte has also an effect even for the same sol.

It would appear from table I that the extent to which the time varies with change in temperature differs with different preparations of the sol. For any particular sol, however, the effect of temperature is approximately the same for the different ions within the roups referred to above.

Experiments were made with freshly prepared sols with excess of arsenious oxide, and the results were similar. In all, fifteen different samples have been used, and the results were always concordant. The experiments with excess of arsenious acid show that the effect of temperature cannot be wholly referred to hydrogen sulphide evolved by the decomposition of arsenious sulphide. It is true that rise of temperature increases the rate of decomposition of arsenious sulphide, but the quantity produced in this way is extremely small. Moreover, the rate of evaporation of dissolved hydrogen sulphide also increases. It would appear from what follows that the effect of temperature is rather complex, and a slight change in the quantity of hydrogen sulphide cannot explain it. It may be pointed out that freshly prepared sols have no perceptible odour of hydrogen sulphide at any of the temperatures investigated, and that the magnitude of the effect observed would require a rather marked change in the concentration of dissolved hydrogen sulphide.

With aluminium sulphate and thorium nitrate, more complicated results were obtained. In some cases, an increase of temperature increases the time, and in other cases the reverse is the case. With a particular sample of the sol and a particular concentration of electrolyte, different readings agreed with one another perfectly. On closer investigation, it was found that concentration of the electrolyte, as well as the quality of the sol, have to be taken into consideration. It must also be remembered that a dilute solution of aluminium sulphate "ages" considerably with time, as pointed out by Powis (*Zeitsch. physikal. Chem.*, 1914, **89**, 106). The combined effect of "ageing" of the sol and the electrolyte will be apparent from table II, in which the time for coagulation diminishes with $1 \cdot 064N/9000$-aluminium sulphate from six and a-half minutes to two and a-half minutes eleven days later, but the influence of temperature is the same in both cases.

TABLE II.

Electrolyte, Aluminium Sulphate.

Concentration.	Sol.	Corresponding times at different temperatures. Room temperature.	25°.	45°.
$1 \cdot 064N/7000$	*I*	3 mins.	2 mins.	$1\frac{1}{2}$ mins.
$1 \cdot 064N/9000$	*I*	$6\frac{1}{2}$,,	—	More than 12 mins.
$1 \cdot 064N/9000$	(11 days later)	$2\frac{1}{2}$,,	—	4 mins.
$1 \cdot 064N/10000$	*I*	6 ,,	—	17 ,,
$1 \cdot 064N/10000$	*D*	15 ,,	—	3 hrs. 28 mins
$N/5000$	*J*	> 2 hrs. 41 mins.	57 mins.	1 hr. 26 mins.

Table III records some similar data with thorium nitrate. Similar irregularities will be noticed here. It would seem that a change in temperature produces independent changes in several factors which govern the mechanism of coagulation.

TABLE III.

Electrolyte, Thorium Nitrate.

Concentration, in grams of the crystallised salt per litre.	Sol.	Corresponding times at different temperatures. 4°.	28°.	6°.
0·025	A	4 mins.	1 min. 30 secs.	More than 2 hrs.
0·02	A_1	11 „	28 mins.	Not in 12 hrs.
0·0175	A_1	31 „	Not in 2 hrs.	—

Sols A and A_1 are of the same sulphide content, but prepared on different dates.

Experiments with Sols containing Ethyl Alcohol and Phenol.

Kruyt and Duin (*Koll. Chem. Beihefte*, 1914, **5**, 269) investigated the effects of adding substances like ethyl alcohol, *iso*amyl alcohol, and phenol, which diminish the surface tension (air–liquid surface) of water. They used them in concentrations varying from $N/50$ to $3N/10$. It is needless to point out that in such concentrations most of the physical properties of the dispersion medium will be altered. Their work has an interesting bearing on the results recorded here in so far as they also found that the bivalent group of cations act in a different manner from the uni- and ter-valent groups. In fact, they observed the reverse effect, namely, an increase in stabilisation with the barium group and a decrease with the rest.

Experiments at three different temperatures with potassium chloride, barium chloride, strontium chloride, calcium bromide, magnesium sulphate, aluminium sulphate, and thorium nitrate were made with sols containing small quantities of alcohol and phenol.

To a definite volume of a sulphide sol was added a definite volume of a solution of alcohol or of phenol of known strength, and in a blank experiment water was added in the same ratio.

With potassium and the bivalent cations exactly the same results were obtained as with the ordinary sols, that is, an increase in stability with rise of temperature for potassium and a decrease in the case of the bivalent cations. The concentration of phenol in the sol was about 0·515 gram in 100 c.c., and that of alcohol varied

from 5 c.c. to 25 c.c. of absolute alcohol in 100 c.c. of the sol. With the small quantities of phenol used, no noticeable change was observed from the blank experiment, but with alcohol a slight decrease in stability for potassium and a slight increase with the bivalent cations were noticed. This is in agreement with the observations of Kruyt and Duin (*loc. cit.*), but the magnitude of the change is small.

With aluminium sulphate and thorium nitrate, more complicated results are obtained, as is to be expected from the temperature-effect with the pure sols, and they will be dealt with on a future occasion.

A few selected data are given in table IV.

TABLE IV.

Electrolyte, Strontium Chloride. Concentration, N/800.

	Corresponding times.		
	0–2°.	28°.	65°.
Sol (with water)	1 hr. 15 mins.	21 mins.	$4\frac{1}{2}$ mins.
Alcohol present	,,	30 ,,	$4\frac{1}{2}$,,
Phenol ,, ...	,,	20 ,,	$3\frac{1}{2}$,,

Calcium Bromide, N/800 *approximately.*

Sol with water	1 hr. 18 mins.	10 mins.	2 mins.
Alcohol present	1 hr. 23 mins.	22 ,,	2 ,,
Phenol ,, ...	1 hr. 15 ,,	13 ,,	About 2 mins.

Magnesium Sulphate, N/600.

Sol with water	35 mins.	7 mins.	2 mins.
Alcohol present	34 ,,	7 ,,	$1\frac{1}{2}$,,
Phenol ,, ...	33 ,,	6 ,,	About 2 mins.

The hydrosol contained 4·8 millimoles of sulphide per litre.

Discussion of Results.

The different effects observed for different ions may be referred to the selective nature of the adsorption process to which a diminution in the charge of the particles of the colloid is due. The different results obtained with different concentrations of the same electrolyte and with different qualities of the sol show the complicated nature of the phenomena. As the theory of the process of coagulation stands at present, the results may broadly be attributed to three factors:

(1) The increase in the number of collisions with increase in thermal energy and decrease in viscosity.

(2) The increase in the repulsive forces between the particles due to a decrease in the dielectric constant of the medium.

(3) Variations in the adsorbability of the different ions present in solution which may change (*a*) the charge of the particles, and (*b*) the adsorbability of the coagulating ions, which necessarily means a change in the coagulating power.

To these must be added any change in the number of the particles and in the total surface of the colloid that may take place with change in temperature. Of these various factors, to which the complex nature of the results may be attributed, (1) has been given a mathematical form by Smoluchowski (*Zeitsch. physikal. Chem.*, 1917, **92**, 129); (2) affects all cases equally, and may be accounted for definitely. Regarding variation of adsorption with temperature, Freundlich (*Zeitsch. physikal. Chem.*, 1906, **57**, 385) gives experimental reasons showing the effect to be slight. This seems to be further supported by the experiments of Burton ("Physical Properties of Colloidal Solutions," 1916, 137), who finds that the mobility of colloidal particles of silver is inversely proportional to the viscosity at different temperatures. This would mean that the charge is constant. The experimental error in his experiments is quite large, and small variations are not ruled out. Since all the other factors affect the different cases equally, it must be concluded that there is a variation in the adsorbability of the coagulating ions to account for the different effects observed with different ions. As there are several opposing factors operating, it is not possible to say whether a decrease or an increase in adsorbability has occurred. If the net result of the other factors is an increase in the stability of the sol, that is to say, a smaller number of successful collisions, then we have to assume that, in the case of potassium or aluminium ions, either (*a*) the adsorbability has decreased, or (*b*) if it has increased, the increase is quite insufficient to counterbalance the stabilising effect due to other causes.

Similar considerations show that nothing can be said as to the direction of change in adsorbability if the net result is in the opposite directions.

In the case of the ions of the barium group and the hydrogen ion, it is evident that the change in adsorbability is relatively more in favour of instabilisation.

However, our ideas regarding the mechanism of this adsorption are vague and indefinite. Even the fundamental assumption that the equality in charge corresponds with a definite rate of coagulation for the different ions is not on very secure ground. There is, of course, much experimental evidence in its favour, but direct experiments on the migration velocity are few. Indeed, Powis

(T., 1916, **109**, 734) obtained a markedly different value of the contact potential for potassium chloride (0·044 volt) from those with other salts (0·026—0·024 volt), corresponding with the same rate of coagulation. What is needed is a more detailed examination of the process of coagulation in all its aspects, and a mathematical formulation of the assumptions made in the simplest form of the theory as developed by Hardy, Freundlich, Bredig, and Smoluchowski.

Summary.

(1) A rise in temperature has different effects on the rate of coagulation, depending on the nature of the electrolyte, the quality of the sol, and the concentration of the electrolyte. These effects are not due to any irreversible change in the sol.

(2) The salts of the alkali metals show a stabilisation at higher temperatures; the salts of the alkaline earth metals always show a diminution in stability, the same being also the case with sulphuric and hydrochloric acids. The same results are obtained even when the sol contains small quantities of alcohol or phenol in solution.

(3) With aluminium sulphate and thorium nitrate, the quality of the sol and the electrolytic concentrations determine the effect of temperature, and both an increase or a decrease in stability is met with, as the case may be. In the presence of traces of alcohol or phenol, the results are more complicated.

(4) Effects of temperature are small compared with the effect of valency, and show that a change in the adsorbability of the different ions must be assumed.

My sincere thanks are due to Prof. F. G. Donnan, F.R.S., for his kind interest in the work and for the facilities for carrying it out. I have also much pleasure in thanking my friend, Dr. J. C. Ghosh.

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XLIV.—*The Preparation of Halogenohydrins.*

By John Read and Margaret Mary Williams.

In a previous communication (T., 1917, **111**, 240), we have shown that when ethylene is passed into cold bromine water, two additive reactions occur simultaneously, leading to the production of ethylenebromohydrin and ethylene dibromide respectively. As the first of these reactions takes place with a greater velocity than the second, the method is well adapted to the preparation of ethylenebromohydrin in quantity. Thus, from 200 grams of bromine reacting in a particular experiment, we were able to isolate 85 grams of ethylenebromohydrin and 88 grams of ethylene dibromide, the corresponding relative percentages of ethylene being, therefore, 59 and 41. The bulk of the ethylene thus reacts to form ethylenebromohydrin rather than to produce ethylene dibromide. Owing to the difficulty of effecting a complete isolation of the bromohydrin, the experiments in question are to be regarded as qualitative rather than quantitative, and the latter aspect is reserved for further treatment.

In a further study of the reaction we have now found it possible to improve the yield of bromohydrin by adopting a modification of the original method, to which, incidentally, we have already directed attention (*loc. cit.*, p. 243), that is, by increasing the concentration of the ethylene, and thus accelerating its gross rate of reaction. At the same time, the modified method reduces the concentration of free bromine in the liquid to a minimum throughout the operation.

A current of air is charged with bromine vapour by causing it to pass slowly through a vessel containing an appropriate quantity of the halogen. The gaseous mixture is then passed through a perforated glass bulb into ice-cooled water, which is subjected to vigorous mechanical stirring throughout the course of the experiment. A second perforated bulb, arranged at a distance from the first, admits a regular stream of ethylene into the liquid in the form of numerous minute bubbles. Reaction occurs readily under these conditions, the bromine being admitted at a rate sufficient to maintain at the most a barely perceptible tint in the liquid. The operation may be conducted for a considerable time, and naturally, in practice, the most effective period will be determined by the influence exerted on the reaction by the steadily increasing concentration of ethylenebromohydrin and hydrogen bromide in the solution. This aspect of the reaction is still under consider-

ation, but it may here be noted that in both the original and the modified method the process was continued until the solution had attained a concentration of somewhat more than 14 per cent. of ethylenebromohydrin, determined by direct isolation, the mean value corresponding approximately with a 1·33N-solution of this substance.

The following results of a typical experiment may be quoted, the products having been separated in the manner already described (*loc. cit.*, p. 242): using 500 c.c. of water, the amounts of ethylenebromohydrin and ethylene dibromide obtained were 82 grams and 54 grams respectively, and the amount of hydrogen bromide present in the liquid at the end was 69·7 grams, estimated by titration. The relative percentage amounts of ethylene corresponding with the above weights of ethylenebromohydrin and ethylene dibromide are 70 and 30 respectively. It is apparent, therefore, that the modified process is superior to the original method in yielding an appreciably higher bromohydrin/dibromide value, the molecular ratio being 1·45 in the original method and 2·3 in the modified process.

As already indicated, the results derived in this manner, although useful for purposes of comparison, are not to be accepted as exact quantitative values, and possibly a more accurate idea of the numerical relationships may be derived from a consideration of the distribution of the bromine in the above experiment. Of the total bromine accounted for (167·3 grams), 62·7 per cent. was utilised in the production of the isolated bromohydrin and 27·5 per cent. was converted to dibromide, whilst the residual 9·8 per cent. represents an apparent excess of hydrogen bromide, the occurrence of which may possibly be due in some measure to decomposition of hypobromous acid into hydrogen bromide and oxygen. Under the conditions now described, however, it seems unlikely that any very appreciable loss of halogen would accrue from this cause; the apparent excess of hydrogen bromide appears rather to be a consequence of the incomplete extraction of the soluble bromohydrin. Accepting this view, that is, adopting the amount of hydrogen bromide formed as a criterion of the yield of bromohydrin, the distribution of the ethylene in the experiment described above would be 75:25, corresponding with a molecular ratio of 3·0 as between ethylenebromohydrin and ethylene dibromide.

Further discussion of these values may conveniently be deferred until further data have been accumulated, but the results prove that cold bromine water provides a valuable source of potential hypobromous acid, and that its application in the manner described opens up a very practical and expeditious method of preparing

bromohydrins. That this additive reaction is capable of wide application is indicated by the results of further investigations, which, however, for the most part have not yet been completed. In the case of cinnamic acid, for example, we have been able to show that a similar reaction occurs with great ease, the ratio of the respective amounts of cinnamic acid converted to bromohydrin and dibromide in a particular experiment being about 5·0 (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 561). Owing to the comparatively high molecular weights of the substances concerned, and also to the ease with which the products may be isolated, the final concentration of bromohydrin in the solution was kept in this case quite conveniently below $0{\cdot}2N$; the high value of the bromohydrin-dibromide ratio is doubtlessly due partly to this factor.

From the results we have recorded in the case of bromine water, it is evident that chlorine water may similarly be regarded as a highly convenient source of potential hypochlorous acid for use in the preparation of the corresponding chlorohydrins. Bromine rather than chlorine was selected for the initial investigation, owing to the reported comparative facility of combination of hypobromous acid with ethylene (*Annalen*, 1866, **144**, 40; *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900), and to the greater convenience of manipulation. Our anticipation that chlorine water and ethylene would react similarly was confirmed by a series of preliminary experiments, but, owing to the pressure of other work, the matter had to be left in abeyance for the time being. The continuation of this line of our investigation has now been rendered unnecessary, owing to the recent publication by Gomberg (*J. Amer. Chem. Soc.*, 1919, **41**, 1414) of the results of a detailed examination of this reaction, the principle adopted being that laid down in our original paper, whilst the amounts of ethylenechlorohydrin produced were estimated by means of a refractometric method which appears to meet adequately the requirements of this particular case. From the results given, it would seem that under comparable conditions the reaction in the case of ethylene proceeds somewhat more readily with chlorine water than with bromine water, interpolation revealing that in the preparation of a $1{\cdot}33N$-solution of ethylenechlorohydrin, the relative percentage amounts of ethylene converted to chlorohydrin and dichloride would be 84 and 11 respectively.

It may be added that a study of the action of chlorine water on cinnamic acid has also given satisfactory results. The details of this last reaction, as well as the results of an extended series of related investigations, are reserved for future publication, but we may remark in this place that sufficient data have been secured to

indicate that both chlorine water and bromine water are capable of wide application in the novel and effective method of preparing halogenohydrins which we have described.

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XLV.—*The Activation of Wood-charcoal by Heat Treatment.*

By JAMES C. PHILIP, SYDNEY DUNNILL, and OLIVE WORKMAN.

THE observation that the absorptive power of wood-charcoal is notably increased by prolonged heating was made by one of the authors in the course of investigations aiming at the improvement of defence against poison gas (see Philip, *J. Roy. Soc. Arts*, 1919, **67**, 126; Winter and Baker, this vol., p. 319). This fact of activation by heat treatment has, however, considerable significance also from the technical point of view, and, further, raises many interesting questions of a purely scientific kind. The present paper contains a brief preliminary record of work carried out with the object of elucidating the extent and the mechanism of the activation effected by heat treatment alone, and divides itself naturally into two parts, which deal respectively with experiments on the absorptive power of wood-charcoal for (*A*) sulphur dioxide, (*B*) methylene-blue in aqueous solution.

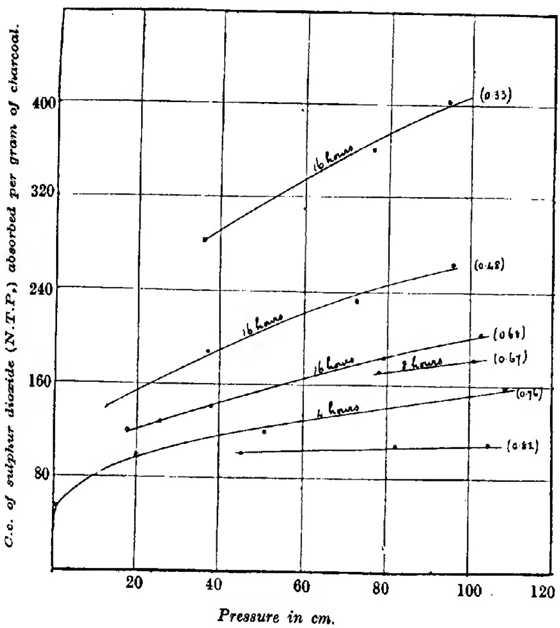
A.

The main series of experiments was carried out with birch-charcoal, and the stock material was prepared by heating small cubes of the wood for three hours at 800°. The product was broken up and screened, the granules which passed through a 0·25 cm. mesh (0·1 inch), but were kept back by 0·125 cm. mesh (0·05 inch), being used in the tests.

For a determination of absorptive power under different pressures, a portion of these granules was placed in a Jena-glass tube which, by means of a T-piece and appropriate stopcocks, could be connected either with a vacuum pump or with a gas-burette containing sulphur dioxide and provided with a long pressure gauge. The tube with the charcoal was first exhausted at a dull red heat for a short time, and then, on cooling, the charcoal was weighed in a vacuum. On putting the glass tube with the char-

coal again in position and immersing it in melting ice, the dead space (of known volume) between the stopcocks and the glass tube was thoroughly exhausted and the connexion with the pump was closed. The sulphur dioxide in the gas-burette was then admitted to the dead space and the charcoal, and equilibrium was allowed to establish itself at a number of different pressures, the volume of unabsorbed gas for each pressure being read off on the gas-burette,

Fig. 1.



with an allowance for the volume of the dead space and the glass tube.

The isothermal volume-pressure relationship thus obtained for the original stock charcoal appears in Fig. 1 as the lowest curve (marked 0·82). The other curves in this figure are the corresponding isotherms (all at 0°) obtained, in the same way as already described, for portions of the stock material which had been heated for the different periods indicated. It is clear that, in general, the absorptive power of the charcoal for sulphur dioxide is increased

by this treatment, but it is equally plain that the duration of the heating is not the main factor in determining the degree of activation.

The clue to this factor is to be found in the alteration of the bulk density which results from the heating of the charcoal (compare Lamb and others, *J. Ind. Eng. Chem.*, 1919, **11**, 427; *Chem. News*, 1919, **119**, 283). Experimental evidence for this is furnished by the figures of the bulk density of all charcoals for which volume–pressure relationships are recorded in Fig. 1. A glance at the values for the *relative* bulk density (added in brackets at the ends of the corresponding curves) shows that the order of activity for birch-charcoals is very nearly the order of the bulk density, and is not determined primarily by the duration of the heating. The conditions under which the charcoal is heated can be widely modified, air being excluded in varying degrees according to the method of packing and covering, and it was proved conclusively that the greater the facilities for the access of air to the heated material, the greater is the decrease of bulk density and the greater the increase in absorptive power. Thus, for example, if a quantity of the original stock charcoal in the form of granules was heated in a crucible for a long period, the portion occupying the bottom of the crucible being separated from the rest by a layer of asbestos, and being thus better protected against circulation of air, it was found that the product from the upper part of the crucible had a lower bulk density and was considerably more active than that from the bottom.

The view that the degree of activation is intimately connected with the extent to which the charcoal is oxidised during the heating is strengthened by experiments made with charcoal from which air was excluded during the exposure to a high temperature. For this purpose, a Jena-glass tube containing a sample of charcoal was freed from air by a current of nitrogen, introduced into an electrically heated furnace, and sealed up about half an hour later. The heating continued for twenty hours, and it was then found that both the absorptive power and the bulk density were practically unaltered. A slight oxidation, even under these conditions, is probably unavoidable, for, as Rhead and Wheeler's work has shown (T., 1913, **103**, 461), it is impossible to heat carbon without getting at least some quantity of the oxides.

Another interesting feature of the curves in Fig. 1 is the change in their character with increasing degree of activation. Whereas with the original, comparatively inactive stock charcoal an increase of pressure above a certain value does not lead to any marked increase of gas absorption, with the most active charcoals there

appears to be no such limit: the slope of the volume–pressure curve becomes steeper as the activation increases.

The observations recorded above appear to be capable of a comparatively simple explanation—an explanation adopted as a working hypothesis by one of the authors (S. D.) during the experimental exploration of the question. According to this view, which differs somewhat from that of the American workers already quoted, the heating of charcoal results in the widening, by progressive oxidation, of the capillary channels with which the granules are riddled. In this way, although the external volume of a granule is practically unaltered, its bulk density is diminished, and the effective surface is enormously increased. For a charcoal of low activity, which, on this view, has extremely narrow capillaries, the deposition of a comparatively shallow layer of gas molecules on the surface will block the capillaries and cut them off from further participation in the absorption process. Increase of pressure in such a case will have very little effect in increasing the absorption, because of the very restricted surface left available. In an activated charcoal, on the other hand, the capillaries have been opened up, and the deposition of additional gas molecules accompanying an increase of pressure can proceed along the walls of these internal capillaries as well as on the free surface of the charcoal. The limit, therefore, of the absorption must lie at a higher pressure than for a charcoal of low activity, and this is what is found experimentally.

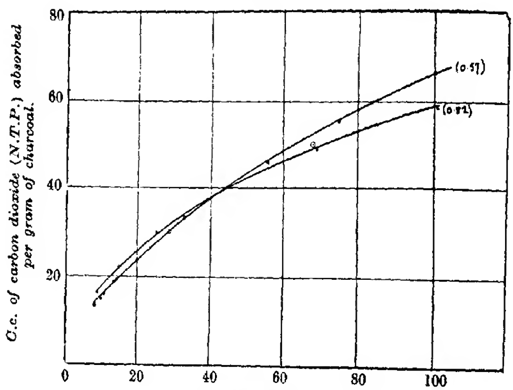
If the foregoing interpretation has any basis in fact, then for low pressures far from the saturation limit, where the molecules of absorbed gas form, presumably, only a shallow layer on the surface of the charcoal, there should be but little difference between activated and unactivated material, even where a notable difference in favour of the activated material develops at higher pressures. This conclusion was confirmed by some experiments on the absorption of carbon dioxide by charcoal at 25°, and the results obtained with two samples of relative bulk densities 0·82 and 0·57, respectively, are shown in Fig. 2. It appears that the charcoal of lower bulk density, although more active at higher pressures, is at lower pressures actually somewhat less absorbent than the unactivated material.

B.

The increase in the absorptive power of wood charcoal for gases effected by continued heating is paralleled by a marked increase in the power of the charcoal to remove methylene-blue from its aqueous solution.

For the purpose of comparing the efficiency of different specimens of charcoal from this point of view, a uniform procedure was adopted. Each sample to be examined was ground in a mechanically-driven agate mortar, and 0·5 gram of the product was then agitated for three hours on a mechanical shaker with a given quantity of a standard methylene-blue solution. Thereafter the solution was filtered, and the residual methylene-blue was determined by titration with titanium chloride. The period of three hours was chosen for the shaking because it was found that, although slight subsequent adsorption of the dye occurred, by far the greater part of the process had been completed in the period

FIG. 2.



mentioned. Moreover, the object was to get a measure of the *comparative* activity of the charcoals, and it was therefore not considered necessary to carry the adsorption to its limit.

The magnitude of the activation effect is shown by the figures given below, which were obtained with Japanese ash charcoal. The wood was first carbonised at 925° for one hour, and a sample of the product (0·5 gram, as in all other cases) was tested for its decolorising power, as described above. The bulk of the product was further heated for eleven hours at 925°, and a sample was again examined. The material was heated subsequently for periods of sixteen, six, eight, and seven hours, in each case at 830°, a sample

being taken and examined at each stage. The results are embodied in the following table:

Total time of heating in hours	1	12	28	34	42	49
Percentage of dye removed from solution	0·6	14·7	24·4	42·5	51·8	60·3

A sample of commercial animal-charcoal, tested under precisely the same conditions, removed 17·8 per cent. of methylene-blue, and it appears, therefore, that the exceptional activity commonly attributed to animal-charcoal can be paralleled, and even surpassed, by a heat-treated wood-charcoal.

Attempts have been made (Glassner and Suida, *Annalen*, 1907, **357**, 95; Knecht and Hibbert, *J. Soc. Dyers and Col.*, 1916, **32**, 226) to correlate the activity of a charcoal in decolorising solutions with its nitrogen content, but the probability of any such relationship must be regarded as exceedingly small in view of the above figures for a wood-charcoal. Further, the charcoal prepared from pure sucrose can be activated in the same way, as was shown by experiments with the original sugar-charcoal employed by Winter and Baker (*loc. cit.*) in their study of the absorption of sulphur dioxide. A sample of this charcoal, tested exactly as has been described, removed only 1 per cent. of methylene-blue from the standard solution. A portion which had been heated at 870° for two hours removed 3·8 per cent., and a portion similarly heated for twenty hours removed no less than 45·4 per cent. of the dye.

The decolorising power of a charcoal appears to be primarily determined by its physical structure and its surface development, and not by the presence of any specific admixture. The efficiency of animal-charcoal itself is a function of the heat treatment it has received, and can be increased to a very notable extent. Thus, the sample of animal-charcoal which, as already stated, removed 17·8 per cent. of methylene-blue from solution, removed 69·6 per cent. after being heated for eighteen hours at about 800°. Special charcoal preparations, such as eponite, exhibit similarly a big increase of decolorising power as a result of heat treatment.

The absorptive power of a charcoal has sometimes been associated with the presence of specific inorganic constituents in the ash, but the results of certain experiments made with Japanese ash charcoal show that this is a factor of very minor significance. The experiments consisted in a comparison of purified and unpurified material, both before and after heating. The unpurified charcoal (*A* in the following table), containing 4·45 per cent. ash, was digested with hydrochloric acid, then thoroughly washed, and dried. This treatment gave a product, *B*, the ash content of which was 1·19 per

cent. The activities of A and B, as well as of the products A_1 and B_1, obtained by heating A and B, respectively, for four hours at about 1000°, are recorded in the table.

Charcoal.	Relative bulk density.	Percentage of methylene-blue removed from solution.
A	—	12·9
A_1	—	31·5
B	0·56	13·2
B_1	0·47	33·2

It is clear that the quantity of the ash makes very little difference either to the original absorptive power or to the degree of activation effected by heating. In harmony, further, with the observations recorded in an earlier part of this paper, the increase of activity is associated with a diminution in the bulk density.

As to the temperature at which the wood or charcoal should be heated to bring about activation, it appears that it must be 800° or above for any rapid improvement to take place. Evidence for this is embodied in the following two tables, in which, it should be noted, each line of figures refers to a portion of the wood (in the form of small cubes) heated independently at the temperature and for the period stated.

Poplar wood at different temperatures.

Temperature.	Duration of heating.	Percentage of dye removed.
370°	2 hours.	0·6
370	5 ,,	0·9
370	17 ,,	1·0
850	2 ,,	5·1
850	5 ,,	11·0

Poplar and willow heated for 2 hours.

Wood.	Temp.	Percentage of dye removed.
Poplar	370°	0·6
,,	850	5·1
,,	1,000	7·5
Willow	300	1·6
,,	600	1·8
,,	850	5·0

The variation in the rapidity of activation with the texture of the original wood was investigated, and it was found that whilst the light woods were activated more rapidly, they were ultimately surpassed in activity by charcoals derived from denser woods, such as box. So far as the more rapid activation of the lighter woods is concerned, the following figures are of interest. The temperature of carbonisation was 850° in each case.

Wood.	Time of carbonisation.	Percentage of methylene-blue removed from solution.
Willow	2 hours.	5·0
,,	5 ,,	18·3
Poplar	2 ,,	5·1
,,	5 ,,	11·0
Box	2 ,,	1·2
,,	5 ,,	2·4

Experiments were instituted with the object of finding whether heat alone, apart from oxidation, would lead to any change in the decolorising power of charcoal, and with this in view, various specimens were heated for a prolonged period in a current of nitrogen. It turned out, however, to be impossible to heat these powdered charcoals without their losing considerably in weight and without considerable quantities of carbon dioxide and carbon monoxide being evolved. The products obtained in this way by heating small quantities of the charcoal at 800° for twenty-four hours were found to have diminished in bulk density and to have gained notably in decolorising power, as is shown by the figures below:

Charcoal.	Loss of weight, per cent.	Relative bulk density.		Percentage of methylene-blue removed from solution.	
		before.	after.	before.	after.
apanese ash	34	0·52	0·41	13·0	38·7
irch	27	0·62	0·48	2·5	16·0
nimal	46	0·41	0·29	17·4	36·4

In view of the pertinacity with which oxygen is retained by harcoal (see Rhead and Wheeler, T., 1913, **103**, 461), it is perhaps iot surprising that appreciable quantities of the oxides should be btained on heating carbon under the conditions stated, but cer-ainly the loss of weight and the increase of activity observed were nuch greater than was expected from the corresponding experi-nents recorded in the first part of this paper. It should, of course, e noted that the charcoal was heated as granules in the one case nd as powder in the other, and it is possible that this explains the lifferent activation effects observed. This and numerous other oints connected with the activation of charcoal by heat treatment till require investigation and elucidation, and further experiments are in progress with this object.

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XLVI.—*The Composition of Salvarsan.*

By Robert George Fargher and Frank Lee Pyman.

Commercial salvarsan is prepared by the reduction of 3-nitro-4-hydroxyphenylarsinic acid by means of sodium hyposulphite, solution of the base in methyl alcohol containing hydrogen chloride, and precipitation of the salt by means of ether (Ehrlich and Bertheim, *Ber.*, 1912, **45**, 756).

It is a yellow, amorphous compound slightly variable in chemical composition and more so in physical properties; chemically, it is generally regarded as 3:3′-diamino-4:4′-dihydroxyarsenobenzene dihydrochloride containing combined solvent, but published statements on the details of its composition contain many discrepancies.

When salvarsan was first introduced into general use, the makers, Farbwerke vorm. Meister, Lucius & Brüning, stated that it contained about 34 per cent. of arsenic. In 1911, however, Gaebel (*Apoth. Zeit.*, 1911, **26**, 215) found that it lost 7·6 per cent. of its weight on heating, and contained only 31·2 or 31·8 per cent. of arsenic. He communicated these results to Ehrlich, with the result that the later circulars of the issuing firm bore the corrected statement: "the arsenic content of the preparation corresponds to the formula $C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$."

The Solvent Content of Salvarsan.

Ehrlich and Bertheim (*loc. cit.*) have given the results of analysis of a specimen of salvarsan prepared, not by the technical method, but by reducing 3-amino-4-hydroxyphenylarsenious oxide with sodium amalgam and acetic acid, as follows:

Found: C=32·63; H=4·06; N=6·06; As=31·99; Cl=15·41.

$C_{12}H_{12}O_2N_2As_2,2HCl,MeOH$ requires C=33·1; H=3·8; N=6·0; As=31·85; Cl=15·07.

$C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$ requires C=30·3; H=3·8; N=6·0; As=31·6; Cl=14·9 per cent.

On determining methyl alcohol in 2 grams of this sample, they obtained a "distinctly positive" reaction, and this fact, in conjunction with the percentage of carbon in the compound, led them to put forward the first of the above formulæ for 3:3′-diamino-4:4′-dihydroxyarsenobenzene dihydrochloride prepared in this way.

Recently, Kober (*J. Amer. Chem. Soc.*, 1919, **41**, 442) has claimed that there is no justification for Gaebel's assumption of $2H_2O$ in salvarsan, and is clearly of opinion that the combined

solvent in salvarsan, precipitated from methyl alcohol by means of ether, is methyl alcohol.

Our experiments show that this view is erroneous. On analysis of two samples of salvarsan precipitated from methyl-alcoholic solution by means of ether, we obtained the following figures:

(*A*) C=29·5; H=4·0; Cl=12·3; S=2·89; As=30·9; ash=0·43; loss in a vacuum=7·6.
(*B*) C=29·2; H=4·1; Cl=12·0; S=2·76; As=31·0; ash=0·79; loss in a vacuum=7·7 per cent.

Determination of the ratio C to As gives the results 5·97 to 1 and 5·89 to 1 respectively, which show that the total carbon content of the product is accounted for by the six carbon atoms of the benzene nucleus attached to each atom of arsenic.

These results contradict Kober's assumption that the combined solvent in salvarsan consists of methyl alcohol, and are confirmed by direct determinations of the methyl alcohol by the method described by Simmonds (*Analyst*, 1912, **37**, 16), and later modified by Jones (*ibid.*, 1915, **40**, 218), when percentages of methyl alcohol varying from nil to 1·4 per cent. were found.*

It may be noted here that when salvarsan is precipitated from methyl-alcoholic solution by means of acetone, the product contains one molecular proportion of acetone, which cannot be removed in a vacuum at the ordinary temperature, and, beyond this, the usual amount of water which can be removed in a vacuum. The acetone was estimated by distilling the compound with water and determining the volume of *N*/10-iodine required to convert the acetone in the distillate into iodoform.†

Mean values found: In air-dried substance, acetone=10·9; loss in a vacuum=6·1; in dried substance, acetone=11·2.

$C_{12}H_{12}O_2N_2As_2,2HCl,C_3H_6O,2H_2O$ requires $C_3H_6O=10·9$; $2H_2O=6·8$.

$C_{12}H_{12}O_2N_2As_2,2HCl,C_3H_6O$ requires $C_3H_6O=11·7$ per cent.

* The method consisted in distilling from an aqueous solution of salvarsan (1 in 20 to 1 in 40), half its volume of liquid and determining methyl alcohol in the distillate. Experiments on the delicacy of the reaction confirmed the figures given by Jones (*loc. cit.*), and indicated that in our experiments as little as 0·2 per cent. of methyl alcohol, expressed in terms of the salvarsan employed, should have been readily detected.

† This method of estimation is the subject of a recent communication by L. F. Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39), who includes a summary of previous literature. The results confirm our experiments on the accuracy and delicacy of the estimation.

The Sulphur Content of Salvarsan.

The presence of a considerable proportion of sulphur in commercial salvarsan—not disclosed in the reputed formula—calls for comment. Ehrlich and Bertheim (*Ber.*, 1911, **44**, 1264; 1912, **45**, 762) mention that crude salvarsan base, prepared by means of hyposulphite, contains inorganic matter and slight quantities of a substance containing arsenic united with sulphur, but indicate that these impurities are removed by converting the base into the hydrochloride. Myers and Du Mez (*U.S.A. Public Health Reports*, 1918, **33**, 1003), and Kober (*loc. cit.*), have recently recorded the bare fact that commercial salvarsan contains sulphur.

Several years ago the present authors (compare Medical Research Committee, *Special Report Series*, No. 44, "Reports of the Special Committee upon the Manufacture, Biological Testing, and Clinical Administration of Salvarsan and its Substitutes," No. 1, p. 8) found that commercial salvarsan of both British and German origin invariably contained sulphur, of which the amount varied from 1 to 2 per cent., and, exceptionally, up to 3 per cent. In our opinion, the sulphur occurs at least in part in the form of the sulphamo-group, $\cdot NH\cdot SO_3H$. Our reasons for this view are as follows:

(1) It is well known that the reduction of nitro-compounds with hyposulphite in alkaline solution leads, sometimes in part and sometimes wholly, to the formation of sulphamic acids of the type $R\cdot NH\cdot SO_3H$. Karrer (*Ber.*, 1915, **48**, 1061) states that "nitrocarboxyphenylarsinic acid does not give the normal arseno-derivative when reduced with hyposulphite, but gives an easily soluble substance, probably a sulphamic acid, as has frequently been observed in other cases." Moreover, in the somewhat analogous case of 3:5-dinitro-4-aminophenylarsinic acid, an alkali-soluble reduction product containing sulphur has been obtained which, on treatment with warm acids, yields free sulphur dioxide and salts of hexa-aminoarsenobenzene (E.P. 8041 of 1913). Although no constitution is assigned in the patent, Giemsa (*Deut. med. Woch.*, 1919, **45**, 95) describes the product as a monosulphamic acid of hexa-aminoarsenobenzene, $HSO_3\cdot NH\cdot C_6H_2(NH_2)_2\cdot As_2\cdot C_6H_2(NH_2)_3$.

(2) Whilst Ehrlich and Bertheim's analysis of pure, as distinct from commercial, salvarsan shows a chlorine content of 15·4 per cent., we have found considerably less chlorine in commercial salvarsan of both British and German origin, the content of samples taken direct from sealed ampoules varying generally from 12·5 to 14·5 per cent. It is thus always lower than that calculated for $C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$, which requires $Cl=14·9$ per cent.,

and, moreover, is usually lower than that necessitated by the neutralisation value (that is, the number of parts of sodium hydroxide required to neutralise 100 parts of salvarsan to phenolphthalein). The difference between the chlorine found on estimation and the quantity corresponding with the acidity of salvarsan must be due to some other acid. The fact that salvarsan forms a sparingly soluble sulphate led us to test for the presence of sulphate in the product, but only negative results, or, at most, indications of traces, were obtained. In view of the evidence of the formation of sulphamic acids in analogous cases, we believe that that part of the acidity of salvarsan which is not due to the hydrochloric acid is due to the presence of the sulphamo-group.

Determinations of sulphur, chlorine, and neutralisation value in ten consecutive preparations, with the results deduced from them, are given below. They are typical of many others.

S.	Cl.	Neut. val.	Cl calculated from neut. val.	Difference in chlorine.	Whence S as $NH·SO_3H$.	Other S.
1·7	14·0	16·45	14·57	0·57	0·51	1·19
1·3	14·1	16 25	14·40	0·30	0·27	1·03
1·26	14·06	16·35	14·50	0·44	0·40	0·86
1·48	13·5	16·36	14·51	1·01	0·91	0·57
1·36	13·8	16·34	14·49	0·69	0·62	0·74
1·44	13·7	16·42	14·54	0·84	0·76	0·68
1·47	13·06	16·45	14·57	1·52	1·37	0·10
1·51	13·66	16·47	14·59	0·93	0·84	0·67
1·77	13·23	16·21	14·35	1·12	1·01	0·76
1·74	13·51	16·35	15·50	0·99	0·89	0·85

The possibility, in the case of salvarsan, of the transformation of the sulphamic acid into a true sulphonic acid would seem to be precluded by the conditions of the experiment, which, from a study of the literature, do not appear to favour the change.

The formation of an internal imide, $R·NH·SO_2·NH·R$, receives, at first sight, support from the low neutralisation values sometimes encountered, but these are more probably due to partial hydrolysis of the dihydrochloride. We have found that reprecipitation of the hydrochloride from methyl-alcoholic solution leads to a product containing rather less chlorine, whilst the chlorine content, when low, is raised by reprecipitation in presence of a further quantity of hydrogen chloride.

Thus, 8·9 grams of 3-nitro-4-hydroxyphenylarsinic acid were reduced in the usual manner, and the resulting base was dissolved in 100 c.c. of methyl alcohol containing 1·13 grams of hydrogen chloride. From a part of the solution, salvarsan was precipitated immediately by the addition of ether (fraction *A*). To 25 c.c. of the remainder a further quantity of 0·2 gram of hydrogen chloride

was added, and the liquor kept overnight before precipitation (fraction *B*). Both fractions were dried under the same conditions and analysed. Found, in *A*, Cl=13·6; in *B*, Cl=14·9 per cent.

Another instance is supplied by a commercial sample of high sulphur content. It contained Cl=12·3; S=3·1 per cent. 1·2 Grams were kept overnight in 10 c.c. of methyl alcohol containing 0·2 gram of hydrogen chloride, and then precipitated by ether. The product contained 13·5 per cent. of chlorine and 2·8 per cent. of sulphur.

(3) Many attempts, both synthetic and analytic, were made to isolate the compound containing sulphur in acid form. Analysis of the commercial hyposulphite employed in the reduction revealed the presence of sulphate, sulphite, thiosulphate, and sulphide as impurities containing sulphur, these, with the exception of sulphide, having been recognised previously by Binz and Sondag (*Ber.*, 1905, **38**, 3830). Increase of the proportion of each in the reduction mixture was without material effect on the sulphur content of the product, and since it was found that the reduction of 3-amino-4-hydroxyphenylarsinic acid with hyposulphite led to a substance containing relatively little sulphur (0·34 per cent.), it was concluded that the acidic sulphur originates during the reduction of the nitro-group by the hyposulphite, a conclusion in harmony with our view of its mode of combination.

Eventually, however, we found that commercial salvarsan, and indeed all specimens prepared by the reduction of 3-nitro-4-hydroxyphenylarsinic acid with hyposulphite, gradually separated to some extent from concentrated methyl-alcoholic solution, this property being much less marked in the preparation obtained by reduction of the amino-acid by hyposulphite and absent in that prepared by the reduction of the amino-acid by hypophosphorous acid. Preliminary examination of the precipitates showed that they contained a greater proportion of sulphur than the parent substance, and were practically insoluble even in excess of methyl alcohol. The isolation of this sparingly soluble portion in a state of comparative purity was accomplished with some difficulty. Ten grams of a specimen of commercial salvarsan (containing Cl=13·7; S=1·0; As=33·0 per cent.) were dissolved in 50 c.c. of methyl alcohol and kept overnight in an inert atmosphere. The deposit was separated centrifugally, very thoroughly washed with methyl alcohol, and dried in a vacuum. It amounted to 0·4 gram of a bright yellow powder, somewhat sparingly soluble in water and insoluble in methyl alcohol. On analysis, it gave the following results:

Found: Cl=6·84; S=5·1; As=30·8*; neutralisation value=15·5.*

The combination of a low chlorine content, a high sulphur content, and a normal neutralisation value prove the presence of acidic sulphur. It may be pointed out, further, that the product approximates in composition to the monohydrochloride of the monosulphamic acid of 3:3′-diamino-4:4′-dihydroxyarsenobenzene, the formation of which would be expected in view of Bertheim's statement (*Chem. Zeit.*, 1914, **38**, 756) that a mixture of two arsinic acids gives on reduction only the unsymmetrical arsenobenzene.

$C_{12}H_{12}O_5N_2SAs_2$,HCl requires Cl=7·3; S=6·6; As=31·1 per cent.; neut. val., 16·6.

The remainder of the sulphur is probably attached to arsenic, this mode of combination being indicated by the fact that the distillate from an acid solution of salvarsan often contains traces of hydrogen sulphide, which can be detected by lead acetate and other reagents, whilst 3-amino-4-hydroxyphenylarsenic trisulphide (D.R.-P. 253157) appears to give up at least part of its sulphur as hydrogen sulphide on boiling with dilute hydrochloric acid.

It should be remembered, however, that salvarsan has been shown to possess some of the properties of a colloid (compare Karrer, *Ber.*, 1919, **52**, [*B*], 2319), and it is therefore possible that a portion of the sulphur unaccounted for by the sulphamo-group may be present in physical association with the compound.

The Preparation of 3:3′-*Diamino*-4:4′-*dihydroxyarsenobenzene Dihydrochloride.*

During the progress of the foregoing experiments, it became necessary to prepare pure, as distinct from commercial, salvarsan.

The reduction of 3-amino-4-hydroxyphenylarsenious oxide to the arsenobenzene by means of sodium amalgam in acetic acid had already been described by Ehrlich and Bertheim (*loc. cit.*), and this and several other modifications involving the reduction of 3-nitro-4-hydroxyphenylarsinic acid step by step were investigated.

The first series of experiments involved the preliminary reduction of the nitro-group without affecting the arsinic acid group, leading to 3-amino-4-hydroxyphenylarsinic acid. This had been accomplished by Ehrlich and Bertheim (*loc. cit.*) by means of sodium amalgam, and we employed this process until it became

* Owing to the small amount of substance available these results are only approximate.

evident that, on repeated use, without elaborate purification, the mercury became contaminated with arsenic and the yield of the amino-acid showed progressive diminution. Several other processes, such as cautious reduction with zinc in acid solution, reduction with ammonium sulphide, and reduction with ferrous hydroxide in alkaline solution, were investigated, and eventually we drew the conclusion that the most satisfactory method was to treat the nitro-acid in cold aqueous alkaline solution with just sufficient hyposulphite to reduce the nitro-group (D.R.-P. 224953; Fargher, T., 1919, **115**, 982). The crude product was contaminated with sulphur, but purification as described by Ehrlich and Bertheim (*loc. cit.*) effected the complete removal of this impurity, an important factor in view of our further experiments.

The reduction of 3-amino-4-hydroxyphenylarsinic acid to the corresponding arsenobenzene was readily accomplished by means of hypophosphorous acid, as follows: Five grams of the acid were dissolved in 25 c.c. of hypophosphorous acid (D 1·15) and 25 c.c. of water, 0·1 gram of potassium iodide being added as a catalyst. The resulting solution was heated to 60° for two hours in an atmosphere of carbon dioxide, cooled, made slightly alkaline with 10 per cent. aqueous sodium carbonate, the precipitated base filtered, washed very completely with water, converted into the hydrochloride by solution in methyl alcohol containing hydrogen chloride, precipitated by dry ether, collected, and dried for several hours in a vacuum. The yield amounted to 3·7 grams. The following figures were obtained on analysis:

Found: As=31·8, 31·84; Cl=14·15; loss in a vacuum=6·38.

In the substance dried at 60° in a vacuum:

Found: C=33·3, 33·0; H=3·6, 3·4; N=6·5.

$C_{12}H_{12}O_2N_2As_2,2HCl$ (439·0) requires C=32·9; H=2·8; N=6·4 per cent.

The base dissolved less readily in methyl alcohol containing hydrochloric acid than did that obtained by the reduction of 3-nitro-4-hydroxyphenylarsinic acid with sodium hyposulphite. The dihydrochloride, grey or very pale yellow in colour, was less readily soluble in water or methyl alcohol than the commercial product. Its solution in three parts of methyl alcohol gave no precipitate on keeping out of contact with air. It decomposed at 187° (corr.).

The reduction of the amino-acid by sodium hyposulphite was also undertaken, the product, in most of its properties, resembling commercial salvarsan rather than the pure substance. It differed, however, considerably in the readiness with which it precipitated

from concentrated methyl-alcoholic solution, and contained only 0·34 per cent. of sulphur. Other figures obtained on analysis indicated a normal composition.

The second series of experiments, conducted by the converse process, namely, reduction of 3-nitro-4-hydroxyphenylarsinic acid to 3:3′-dinitro-4:4′-dihydroxyarsenobenzene and subsequent reduction of the nitro-groups, was less successful.

The first stage was readily accomplished by means of hypophosphorous acid essentially as described in D.R.-P. 269886, although the somewhat elaborate precautions taken in isolating the product to ensure freedom from the corresponding diamine were found to be superfluous, since the reduction of the nitro-group by the addition of potassium iodide to the reduction mixture (D.R.-P. 271894) could not be confirmed.

Owing to its insolubility, dinitrodihydroxyarsenobenzene could not be reduced with sodium amalgam in acetic acid solution, and although in alkaline solution reduction took place readily, the product was unsatisfactory. The base obtained by reducing dinitrodihydroxyarsenobenzene in alkaline solution with sodium hyposulphite proved somewhat difficult to filter and wash. The hydrochloride prepared from it differed but little from commercial salvarsan.

In conclusion, we are glad to have the opportunity of recording that this work was carried out in collaboration with the technical experts of Messrs. Burroughs Wellcome & Co., and to thank especially Dr. H. A. D. Jowett and Mr. F. H. Lees, F.I.C., for their valuable help and advice in the course of the work.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
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XLVII.—*The Solubility of Potassium Bromide in Bromine Water.*

By ALFRED FRANCIS JOSEPH.

In a paper communicated to the Society in 1913 (T., **103**, 1554), figures were given for the solubility of potassium bromide in nitrobenzene solutions of bromine. It was there shown that whereas this salt is practically insoluble in pure nitrobenzene, a considerable amount could be dissolved in the presence of bromine, owing to the

formation of the readily soluble tribromide, for the existence of which colorimetric evidence was adduced.

In continuation of these experiments, a study of the corresponding aqueous solutions (saturated with respect to potassium bromide) was commenced. This work was, however, interrupted five years ago, and as it is not likely to be resumed, the results obtained are now published.

Solutions saturated with respect to bromine have been studied by Worley (T., 1905, **87**, 1107) for potassium bromide and by Bell and Buckley (*J. Amer. Chem. Soc.*, 1912, **34**, 14) for sodium bromide. For solutions of moderate concentration, the solubility of bromine was found to be greater in bromide solutions than in pure water by approximately one gram-molecule of bromine for each molecule of bromide, and it was shown that this is in accordance with the formation of a tribromide. In the case of concentrated solutions of sodium bromide, however, the ratio of additional bromine to bromide rose to nearly 2·5 : 1, indicating the formation of a higher polybromide.

In the experiments now recorded, the solubility of potassium bromide in bromine water was determined by shaking bromine, water, and an excess of potassium bromide in 250 c.c. stoppered bottles in a 50-litre thermostat provided with a Noyes shaking arrangement for twenty-four hours, the temperature being maintained at 32·4 ± 0·02°.

Solubility of Potassium Bromide in Water.—Several results for the solubility of potassium bromide in water are given in the literature, but they differed sufficiently to make its redetermination worth while at the exact temperature at which these experiments were to be made.

Kahlbaum's best potassium bromide was used, without further purification beyond drying at 150°. It showed only a trace of chloride (less than 0·05 per cent.) when tested by Caven's method of distillation with nitric acid (*J. Soc. Chem. Ind.*, 1909, **28**, 505). The determination was carried out as usual, and the results, expressed as grams of potassium bromide dissolved by 100 grams of water, were:

(*a*) 72·53	(*b*) 72·67	Mean ... 72·56
(*c*) 72·58	(*d*) 72·47	

The figure given in Seidell's "Dictionary of Solubilities," obtained by interpolation between 30° and 40°, is 71·8. Coppet (*Ann. Chim. Phys.*, 1883, [v], **30**, 416) and Etard (*Compt. rend.*, 1884, **98**, 1432) found that the solubility of potassium bromide was a linear function of the temperature, according to the formula of

the former, the result at 32·4° should be 71·05, and according to the latter 73·43; the value here recorded is very nearly the mean of these.

Solubility of Potassium Bromide in Bromine Water.—In these experiments, a portion of the solution was dropped into a flask containing concentrated potassium iodide solution, the flask and contents being weighed before and after the addition of the bromine–bromide solution. The iodine liberated was determined by titration with sodium arsenite solution standardised against pure iodine. The remainder of the solution was then transferred to a warm cylinder in the thermostat and its density determined approximately by means of the Westphal balance; the figures are probably correct to ±0·0003.

The results are given in the table below.

Grams of bromine per 1000 grams of water.	Grams of potassium bromide per 1000 grams of water.	Density.	Grams of bromine per litre.	Grams of potassium bromide per litre.
0·0	725·6	1·3917	0·0	585·1
24·0	733·9	1·4063	19·2	587·1
32·1	738·2	1·4070	25·5	586·7
39·6	740·7	1·4132	31·4	588·0
74·3	750·2	1·4356	58·4	589·9
120·9	764·3	1·4633	93·8	593·2
137·2	771·1	1·4753	106·1	596·2
229·7	801·3	1·5236	172·3	601·1
382·1	845·9	1·5980	274·1	606·7

Results.—The numbers in the first two columns are related by the straight line formula: increased solubility of potassium bromide = one-third of the bromine concentration.

If A and B are the total molecular concentrations of bromide and bromine per 1000 grams of water, and S is the solubility of bromide in water alone, the equation is

$$(A-S)/B=0{\cdot}47.$$

The actual values of the fraction found for the eight determinations are:

0·50	0·53	0·44	0·44	Mean ... 0·47
0·53	0·46	0·45	0·42	

The corresponding ratio for nitrobenzene solutions was found to vary from 0·53 to 0·32, indicating a much less close agreement with a linear relationship.

If there were no disturbing factors, the ratio should be calculable as follows, on the assumption that the increase of solubility is due to the formation of potassium tribromide.

In the dissociation equation for the tribromide,

$$k(KBr_3) = (KBr) \times (Br_2),$$

the concentration of the free bromide is constant (S) as the solution is saturated with respect to it; that of the tribromide, obtained by subtracting the former from the total concentration of bromide, is $A - S$, and the free bromine by subtracting this last from the total concentration of bromine, that is, $B - (A - S)$, so that $k(A - S) = S(B - A + S)$, or $(A - S)/B = S/(k + S)$, a constant.

For nitrobenzene solutions, k and S are very small, and neither is known, so that this constant cannot be evaluated. For aqueous solutions, S is 6·1 and k, determined by various methods, about 0·05 (Roloff, *Zeitsch. physikal. Chem.*, 1894, **13**, 327; Worley, *loc. cit.*; Joseph and Jinendradasa, T., 1911, **99**, 274), so that $S/(K + S)$ is a little less than unity.

If this held, nearly one gram-molecule of bromide should pass into solution for every gram-molecule of bromine present. The fact that the actual amount dissolved is only about half a gram-molecule shows clearly enough that a disturbing factor is present, but whether it is reduction of solubility of potassium bromide in water by the common ion of potassium tribromide, or the hydration of bromine, causing a reduction in the amount of "free" bromine, or some other cause, has not been investigated.

Very Concentrated Solutions.—It was hoped to extend these experiments to the study both of very dilute and of very concentrated solutions. Preliminary work on the latter was carried out as follows.

About 250 grams of potassium bromide, about the same weight of bromine, and enough water for the experiment (the amount in different experiments varied from 5 to 100 c.c.) were left in a stoppered bottle for a few days at the ordinary temperature (28°), after which the heavy, dark liquid was filtered through glass wool and analysed.

The results of two such experiments are given below.

	Percentage by weight.		Grams per 1,000 grams of water.		Grams per litre of solution.	
	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.
Water	13·5	5·4	1000	1000	347	154
Bromide	28·4	15·1	2104	2796	738	432
Bromine	58·1	79·5	4304	14720	1511	2274
Density	2·596	2·860	—	—	—	—

Potassium bromide appeared to be quite insoluble in pure bromine, and it must therefore be concluded that the water is entirely responsible for keeping these large quantities in solution;

the limit of solvent capacity of the water, even when it constitutes only 5 per cent. of the solution, has not been reached.

So far as the volume concentration (grams per litre of solution) is concerned, the maximum for the bromide has been passed before the water is reduced to this extent; the concentration of bromine corresponding with this maximum must lie somewhere between 200 and 2000 grams per litre.

Conclusion.—(*a*) The solubility of potassium bromide in water is increased by the addition of bromine. For moderate concentrations, about half a gram-molecule of bromide is dissolved for each gram-molecule of bromine added to the water.

(*b*) The limit of the solvent capacity of the water was not reached at bromine-concentrations of more than 2000 grams per litre. There is, however, a maximum volume-concentration of bromide, the corresponding bromine-concentration being somewhere between 200 and 2000 grams per litre.

These experiments were carried out in 1914—1915 at the Ceylon Medical College, and my thanks are due to Mr. W. N. Rae for kindly making the measurements with the hydrostatic balance.

WELLCOME TROPICAL RESEARCH LABORATORIES,
KHARTOUM.

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War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 18TH, 1919.

By JAMES WALKER.

I NEED not say how greatly honoured I feel by the invitation of the Council to deliver one of the lectures connected with the War which are to be given in the present session. The title of my lecture is that suggested by the Council, and the experiences I am about to relate are my own, or rather those of my colleagues, for my part was largely that of an interested spectator. These experiences, however, must have been to a great extent shared by all those engaged on the same problems. I therefore make no claim, on behalf of myself or my colleagues, for any novelty of process or method; indeed, one of the most pleasing features of the explosive manufacture during the war was the pooling of results, whereby each factory derived the benefit of the experiences, not only of other factories, but of the Research Department of the Royal Arsenal, Woolwich, and later also to some extent of the Munitions Inventions Department.

In the early spring of 1915, when the dearth of high explosives was the occasion of public outcry, we in the Chemistry Department of Edinburgh University felt that we might do something to utilise local supplies for the production of trinitrotoluene. The War Office was approached, and the suggestion was favourably received by Lord Moulton, the Director of Explosives Supply, to whom we owe most grateful thanks for constant encouragement and help in our enterprise. A company, named the Lothian Chemical Company, which consisted of Dr. A. C. Cumming, Mr. J. W. Romanes, and myself, was formed to execute a contract for the supply of 150 tons of T.N.T., without the use of fuming sulphuric acid, within a specified time, and work was begun in April, 1915, in a disused chemical factory. The management and staff of the factory were recruited from teachers, graduates, and undergraduates of the University Chemistry Department. The first dispatch of T.N.T. was made in October, 1915, and the contract was completed well within the specified period. Further contracts followed, but as the factory was incapable of any great extension, and was, besides, unsuit-

ably situated in a populous district, we agreed to undertake for the Ministry of Munitions the erection and management of a larger factory in the outskirts of the city, known as H.M. Factory, Craigleith. This factory was originally designed to produce 30 tons of T.N.T. per week, but during construction was expanded to manufacture 50 tons weekly. Production was begun in March, 1917, and by July of the same year 30 tons weekly were being delivered. The manufacture of T.N.T. in the original factory was then discontinued, and the works, after considerable delay, were turned over to the manufacture of calcium nitrate. At the date of the armistice, H.M. Factory, Craigleith, was producing as a maximum 60 tons of T.N.T. weekly.

In this country, sodium nitrate from South America was practically the only source of nitric acid and other nitrates. With the progress of the war, however, the consumption of nitrates continually augmented, and the difficulty of importing nitrate from overseas increased owing to the lessened freightage and submarine risks. It became therefore of the utmost national importance first to economise nitric acid by carrying processes of recovery to the highest possible point of efficiency, and secondly to find home sources of nitrates. It may be said that the first problem was adequately solved, but the solution of the second was only in its initial stage at the conclusion of the war.

Manufacture of Nitric Acid.

1. *From Sodium Nitrate.*

The method we adopted for the manufacture of T.N.T. was a two-stage process, toluene being nitrated first to a degree intermediate between mononitrotoluene and dinitrotoluene, the product being thereafter fully nitrated to trinitrotoluene by the use of concentrated nitric acid and concentrated sulphuric acid. The residual acids from the final process were employed in effecting the first nitration. The nitric acid used was made in the customary way from sodium nitrate and sulphuric acid, and was collected at different strengths, according to the requirements of nitration. Thus at one period seven-tenths of the nitric acid was collected as 94 per cent., and three-tenths as 70 per cent., acid; towards the end of the war nine-tenths was collected as 90 per cent. acid and one-tenth as 60 per cent. acid. The concentration of sulphuric acid employed was generally 92 per cent., 2·6 tons of this acid being used for a charge of 2·75 tons of crude sodium nitrate. The distillation occupied about fifteen hours, but was on occasion carried through in eight. The nitre cake from the stills

contained, on the average, 28 per cent. of potential sulphuric acid and only a trace of nitrate. The loss in manufacture was from 5 to 6 per cent.

[Slides of the plant employed were exhibited, and attention was directed to the valuable work of the Thermal Syndicate in supplying the silica condensing spirals and connexions, which greatly facilitated the manufacture.]

2. *From Ammonia.*

Catalytic oxidation of ammonia by Ostwald's method was the most readily available process for the production of nitric acid and nitrates from home material. Of this process we had a brief and incomplete experience, owing to delay in its adoption on a manufacturing scale.

When ammonia is oxidised by air on the surface of a solid catalyst, such as platinum or ferric oxide, the following main reactions take place:

I. $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.
II. $4NH_3 + 5O_2 = 4NO + 6H_2O$.

[Experiments with a platinum wire catalyst were shown which illustrated the prevalence of one or the other reaction according to the proportion of ammonia and air taken.] The concentration of ammonia in the ammonia-air mixture which gives the most favourable results with platinum lies between 10 and 12 per cent., variations within this limit affecting the yield of nitric oxide but little. On a small scale, a yield of 97 per cent. of the theoretical quantity of nitric oxide was obtained.

The source of ammonia which we employed was 25 per cent. purified ammonia liquor, from which the gas was liberated by steam in an ammonia still of the rectifier type. The ammonia gas was passed through a cooler, then through an iron oxide purifier to remove sulphur compounds, and was finally mixed with air, which was supplied by a blower and measured by passage through a meter. The amount of ammonia in the mixed gases was regulated by the feed of ammonia liquor to the still. Thorough mixing was effected in a chamber provided with baffle plates, and the proportion of ammonia in the mixture was checked by analysis as occasion required. In order to protect the platinum catalyst from dust, and especially from particles of iron rust, which greatly lower its efficiency, the air-ammonia mixture before entering the converter was filtered through a box containing slag wool or glass wool.

The converter containing the catalyst was of the type suggested by the Munitions Inventions Department.* It consisted of a square aluminium box of 30 cm. side, built in sections, and connected by pyramidal adapters to aluminium tubes conveying the gases from beneath and leading them off above. Across this aluminium box was placed horizontally a screen of platinum wire gauze of 32 meshes to the cm., the diameter of the wire being 0·06 mm.

Trials were made with one, two, and three successive gauzes in close proximity to each other, but no definite conclusion as to the best arrangement had been drawn before stoppage of the operations. The catalyst, activated by previous heating, was warmed at one spot by means of a flame. The heat produced by the catalytic oxidation at this spot gradually spread and raised the temperature of the whole gauze until it reached 650° to 700°, when it remained steady. The time taken by the gases to pass through one thickness of gauze was of the order of one-thousandth of a second, and the temperature of the gases passing from the converter was about 400°. The impurities in the by-product ammonia used seemed to have little effect on the catalytic activity of the platinum.

The next operation was to convert the nitric oxide thus produced into nitric acid by means of atmospheric oxygen and water:

$$4NO + 3O_2 + 2H_2O = 4HNO_3.$$

The hot gases issuing from the converter were first passed through wide silica **S**-pipes cooled by a stream of water, and then through pipes of narki metal (iron–silicon alloy) completely immersed in water. The temperature was thereby reduced to about 30°, and the gases passed into the oxidation and absorption towers, which were in principle the same as those used in the recovery of nitrous fumes, to be described in the next section. The first absorption towers were acid towers, and these converted the great proportion of the nitrous gases into nitric acid. The final towers were fed with milk of lime, which yielded the remaining oxidised nitrogen as a mixture of calcium nitrite and nitrate. This mixture was returned and fed, along with water, to the first towers in order that the nitrite it contained might be converted into nitrate by means of the nitric acid formed in these towers, the nitrous fumes evolved passing further along the series and being subject to further oxidation. The nitric acid ultimately collected from the acid towers was converted by neutralisation with milk of lime into

* A description and figure of a smaller type may be found in a report of the Ministry of Munitions entitled "The Oxidation of Ammonia Applied to Vitriol Chamber Plants," London, 1919.

calcium nitrate, which was finally concentrated to the required extent in evaporating pans. At the date of the armistice we had only passed out of the experimental stage and begun large-scale production, 30 tons in all having been made.

Recovery of Nitrous Fumes.

The question of economy of nitric acid in the production of T.N.T. is largely dependent on the recovery of nitrogen contained in the waste acid of the nitrating process in a form suitable for its return to the process. The practical importance of the recovery may be estimated from the following table, which exhibits the amount of nitric acid used for the production of 1 ton of T.N.T. and illustrates the continued improvement of the recovery:

June, 1917 (no recovery)	1·27 tons
December, 1917	1·19 „
June, 1918	1·05 „
September, 1918	0·955 „

Without recovery, one-third more acid was required per ton of manufactured product than with effective recovery.

The first section of the recovery plant [which in the lecture was illustrated by numerous slides] consisted of denitrators, various types of which were tested, that finally adopted being on the principle of a rectifying still. Each denitrator was constructed of acid-resisting brick, was square in section, and was divided into six compartments by finely perforated earthenware plates (malting tiles), through each of which passed a wide overflow pipe dipping into the acid of the section beneath. The waste acid from the settling tanks was fed to the topmost section, and the denitration was effected by steam introduced into the lowest section. The steam passed upwards through the small perforations, and thus bubbled through the acid lying on the plates, heating and diluting it and depriving it of the nitric acid and nitrous compounds which it contained. The acid as it accumulated on each plate flowed downwards through the wide overflow pipe. No air was used in the denitration. Three units were employed, which together recovered 2 tons of nitric acid per day. The average percentage composition of the waste acid entering and leaving the denitrator was as follows:

	Sulphuric acid.	Inorganic nitrogen, calculated as nitric acid.
Waste acid	69·8	5·34
Denitrated acid	66·3	0·1 (maximum)

The denitrated acid passed to sulphuric acid concentrators, and the gases from the denitrators to silica cooling spirals, which con-

leused the issuing steam and nitric acid to a dilute nitric acid olution, afterwards fed to the recovery towers. The cooled, un-ondensed nitrous gases passed into wide earthenware mains, in vhich they were mixed with excess of air. The mixture was then ed into a large brickwork chamber to afford time for oxidation to ake place. Thence the gases passed to a series of six recovery owers, 90 cm. in diameter and 5 m. high, packed with earthen-vare rings to secure proper distribution of liquid and gas. In ach tower the gas entered below and met the descending liquid. The solution withdrawn at the foot was raised by means of Pohle ir-lifts to a distributing vessel at a level above the top of the owers. From this the solution could be passed once more down he same tower, or on to the next tower of the series, in any roportions that might be desired.

This arrangement conferred a flexibility on the plant which was ound useful. What strikes an academic chemist when he first omes into contact with works plant is its rigidity. He is accus-omed to adaptable glass and rubber, and meets with inflexible netal and earthenware. A plant is usually designed on the ssumption that the process will always go right—an assumption y no means well founded. Occasionally things go wrong, or a ariation has to be made in the mode of working; then the rigidity f the plant shows its undesirable features. Alternative con-exions may often without difficulty be introduced to obviate this, nd even glass and rubber may find suitable employment on a vorks scale.

The series of towers was worked on the counter-current principle, he nearly exhausted gas coming into contact in the last tower of he series with dilute nitric acid from the denitrator condensers, o which water was added as required. The total free volume of he towers with their wide connecting pipes was about 28 cu. netres, and the time occupied by the gas in passing through the eries was about five minutes.* Induced draught secured the teady flow of gas through the system. Cooling the liquids (and onsequently the gases) as far as possible was of prime importance n the recovery, and this was largely effected in the air-lifts. The ssuing gas contained 8 to 10 per cent. of oxygen. The nitric cid solution obtained at the base of the first tower varied between 54 and 62 per cent., in accordance with the requirements of the itration process, to which it was returned. The recovery by neans of this system of denitrators and towers was more than

* Compare an article on "The Theory of Absorption Towers for Nitric Acid Manufacture," by J. R. Partington and L. H. Parker (*J. Soc. Chem. Ind.* 1919, 38, 75).

93 per cent. of the inorganic nitrogen delivered to the denitrators in the waste acid.

The following table shows the destination of the nitrogen supplied to the T.N.T. plant as sodium nitrate, the figures being for the month of September, 1918:

Loss in nitrate bags, handling, etc.	...	0·98 per cent.
Loss in manufacture of nitric acid	...	5·42 „ „
Loss in nitration, washing, and packing...		9·91 „ „
Loss in denitration...	... ...	2·03 „ „
Total loss	...	18·34 per cent.
Sent out in T.N.T.	...	81·66 „ „
		100·00 per cent.

We were greatly pleased to receive in November, 1918, communications from the Department of Explosives Supply stating that the figures in nitrogen economy during the two months of September and October constituted a record for the country, and asking us to congratulate the staff on the result, in which connexion I especially desire to mention the name of the Chief Chemist at Craigleith, Mr. Donald Grant. The figures quoted by no means exhausted the possibilities of economy, and it is certain that if the production had continued, an immediate further saving of at least 2 per cent. would have been effected, the alterations on plant necessary to secure this being practically ready at the date of the armistice.

If I may draw a moral for the academic chemist from our experience, it is that he need not fear to enter chemical industry provided he has common sense, energy, a competent knowledge of his subject, and a willingness to co-operate with engineers and men of technical experience. These qualities suffice for any chemical routine manufacture, and if he is possessed, in addition, of far-sightedness and a spark of imagination, he may, I think, venture with confidence on novel methods and new chemical industries. I am, of course, only speaking of the manufacturing side of the problem; the business side is of equal or greater importance. In Edinburgh we had no commercial difficulties; our supplies and our market were alike assured. Business training and collaboration with business men is on the part of the directing chemist essential if the enterprise is to be a commercial success.

There is, I think, at the moment a current, or perhaps an undercurrent, of belief that with the establishment of research laboratories in connexion with the various industries of this country all will necessarily be well with those industries. This opinion I do not share. Research laboratories, although indispensable, are not

in themselves sufficient to secure success in the chemical or any other manufacture. The admirable research laboratories of the German chemical works should, to my mind, be regarded rather as a noteworthy feature of the general excellence of German scientific business organisation than as the prime cause of success of the German chemical industry.

XLVIII.—*The Influence of Position on the Boiling Points of Isomeric Benzene Derivatives.*

By Nevil Vincent Sidgwick.

In a previous paper (Sidgwick, Spurrell, and Davies, T., 1915, **107**, 1202) it was shown that whilst the curves of solubility in water of the three cresols, and similarly (above their triple points) those of the three toluic acids, lie very close together, the relations are quite different with the three nitrophenols, the ortho-compound being far less soluble than either of the other two, the solubilities of which are almost identical. It was suggested that this might be due to some intramolecular rearrangement taking place either in the ortho- or in the meta- and para-nitrophenols, so that they are not really all of the same type; since the behaviour of the cresols and the toluic acids showed that, where such rearrangement is impossible, or at least improbable, the influence of position on the solubility is very small. It was further pointed out that this abnormality of the nitrophenols extends also to the boiling point, the ortho-compound boiling some 80° lower than the para-, whereas the normal difference in boiling point between position-isomerides does not exceed a few degrees. It is remarkable that it is the more volatile compound which is the least soluble in water, although one would expect the reverse to be the case.

It is obviously of interest to inquire how far this abnormality of behaviour, with respect to solubility and vapour pressure, extends, and especially to determine how its occurrence is related to the chemical nature of the substituent groups. As regards the solubility, the data afforded by the literature give comparatively little assistance; but the boiling points have been recorded for a large number of benzene derivatives, and their examination leads to results of some interest.

In order to avoid error due to unconscious selection, all the boiling points of di- and poly-derivatives of benzene given in the

last edition of Richter's "Lexikon" were collected and classified according to the chemical nature of the substituents. Their use is considerably restricted by the absence of any agreement among chemists as to the pressure (other than atmospheric) at which boiling points should be observed, and the impossibility of applying any temperature-correction amounting to more than a few degrees. Even so, there remain some 500 sets of isomerides the boiling points of which are recorded under comparable conditions. The numbers are, of course, liable to considerable errors; the temperatures are frequently uncorrected, often the isomerides have been examined by different observers at different times, and it is likely that in some few instances much larger errors may have been introduced by the incorrect identification of the compounds investigated.

In spite of these difficulties, the analysis of the data shows in a sufficiently striking manner that the differences in the boiling points of isomeric derivatives vary over a wide range, and that their magnitude is closely related to the chemical nature of the substituent groups.

The simplest way of expressing the results is by means of the "greatest difference," that is, the largest difference in degrees between the boiling points (under the same pressure) of any two of the three isomerides. Taking the substituents which are least likely to undergo rearrangement—the alkyl and alkylene groups—it is found that among the di-derivatives, out of fourteen examples the maximum value of the greatest difference is 19° and the mean 7·6°, or, excluding two instances, the maximum is 13° and the mean 5·8°. Among the tri-derivatives, we find: out of 7, maximum 18° mean 7·0°, or, excluding one, maximum 11°, mean 5·2°.

We may therefore assume that a change in the position of an alkyl group does not alter the boiling point by more than 10°. This enables us to extend the basis of our induction by including those tri-derivatives in which one at least of the substituents is an alkyl or alkylene group, since the position of this group will have little effect on the boiling point.

The following tables are drawn up on this principle. In table I the two substituents are given first, then the number of sets of isomerides coming under this head, then the maximum and mean values of the "greatest differences" in boiling point. This is then given for the tri-derivatives, it being understood that the third substituent is always an alkyl group. When two sets of figures are given under one heading, the second is arrived at by excluding one or two extreme values, as being probably due to experimental error. In table II the results for the di-derivatives are summarised the mean values alone being quoted. In this table a class of com

pounds with two different substituents occurs twice, once under each of its two groups.

The abbreviations mostly explain themselves. "Alk." stands for an alkyl or alkylene group; "NHX" for an amine group with one substituent other than an alkyl.

TABLE I.

Substituents.	Di-derivatives. No.	Di-derivatives. Max.	Di-derivatives. Mean.	Tri-derivatives. No.	Tri-derivatives. Max.	Tri-derivatives. Mean.
Alk. : Alk.	14	19°	7·6°	7	18°	7·0°
	12	13	5·8	6	11	5·2
Alk. : Ester	8	22	8·1	3	11	5·0
	7	10	6·0	—	—	—
Alk. : Ether	25	23	7·9	6	23	11·5
	24	11	7·3	4	12	6·0
Alk. : Halogen	12	14	6·3	13	11	6·3
Alk. : CH	6	15	10·0	4	13	9·2
Alk. : C_nH_{2n}·OH	3	7	6·0	2	13	9·0
Alk. : SH	1	—	2·0	2	5	3·5
Alk. : NH_2	6	10	5·2	2	14	13·0
Alk. : C_nH_{2n}·NH_2	3	10	4·0	—	—	—
Alk. : NHAlk.	4	5	3·4	2	14	12·0
Alk. : NHX	7	12	9·3	—	—	—
Alk. : CN	3	14	6·0	2	13	9·5
Alk. : CHO	1	—	5·0	1	—	10·0
Alk. : OAcyl	4	9	6·5	2	9	8·5
Total	98	23	6·85	45	23	8·2
	94	15	6·3	42	14	7·3
Alk. : NO_2	3	26	20·3	2	48	44·0
Alk. : $NAlk_2$	2	32	27·0	1	—	36·0
Alk. : CO·Alk	2	19	15·5	6	25	12·0
Alk. : CO_2H	1	—	15·0	1	—	8·0
Alk. : CO·$N(CH_3)_2$	1	—	37·0	—	—	—
Aryl : Halogen	2	14	13·5	—	—	—
Aryl : OH	1	—	33·0	—	—	—
Aryl : NH_2	1	—	48·0	—	—	—
OAlk. : OAlk	6	17	6·5	3	33	14·7
	5	9	4·4	2	11	5·5
OAlk. : Ester	6	25	16·0	4	15	9·0
OAlk. : Halogen	8	13	17·6	1	—	32·0
OAlk. : OH	2	39	34·5	5	26	15·8
OAlk. : C_nH_{2n}·OH	4	15	12·8	1	—	7·0
OAlk. : NH_2	3	40	33·0	3	30	23·0
OAlk. : CN	2	12	6·0	—	—	—
OAlk. : CHO	2	18	14·5	4	17	9·5
OAlk. : OAcyl	2	17	11·0	—	—	—
OAlk. : NO_2	2	19	13·5	2	30	19·7
OAlk. : CO·Alk	3	18	12·3	5	18	8·2
Ester : Ester	2	17	9·0	—	—	—
Ester : Halogen	4	15	7·5	—	—	—
Ester : OH	2	66	33·0	2	59	33·5
Ester : NH_2	1	—	30·0	—	—	—
Halogen : Halogen	2	17	9·0	4	29	14·0
	—	—	—	3	12	9·0

TABLE I. (*continued*).

Substituents.	Di-derivatives. No.	Max.	Mean.	Tri-derivatives. No.	Max.	Mean.
Halogen : $CH_2\cdot OH$ ...	1	—	7·0	—	—	—
Halogen : OH	2	44	43·5	2	44	42·0
Halogen : NH_2	2	26	13·0	2	22	19·5
Halogen : NHAlk.......	1	—	24·0	—	—	—
Halogen : NHAcyl ...	2	30	25·0	—	—	—
Halogen : $NAlk_2$	2	27	26·0	—	—	—
Halogen : NO_2	3	7	5·3	2	25	19·0
Halogen : CHO	2	10	7·5	—	—	—
Halogen : COCl	3	24	15·7	—	—	—
Halogen : CN	2	27	17·5	—	—	—
OH : OH	1	—	34·0	1	—	36·0
OH : NO_2	1	—	80·0	—	—	—
OH : CHO	1	—	43·0	1	—	20·0
OH : $CO\cdot CH_3$	—	—	—	1	—	68·0
NH_2 : NH_2	1	—	26·0	1	—	29·0
NH_2 : NHAlk.	2	27	23·5	2	13	11·5
NH_2 : $NAlk_2$	2	51	33·0	1	—	24·0
NH_2 : CO·Alk.	1	—	47·0	—	—	—
NH_2 : CN	1	—	24·0	—	—	—
NHAlk. : NHAlk.	1	—	29·0	—	—	—
NHAlk. : $NAlk_2$.........	1	—	15·0	—	—	—
$NAlk_2$: $NAlk_2$	1	—	50·0	1	—	32·0
NO_2 : NO_2	1	—	19·0	—	—	—
NO_2 : CO·Alk...........	1	—	20·0	—	—	—
COCl : COCl	1	—	23·0	—	—	—

Summarising these results, we find that the compounds may be divided into three groups.

I. *Difference of Boiling Points less than* 10°.—These may be called the normal compounds. They include the following substituents: alkyl groups alone, or one or more alkyls with an ester, alkyloxy-, alcohol, halogen, aldehyde, amino-, monoalkylamino-, or hydroxyl group; also two alkyloxy- or one alkyloxy- and one halogen, two halogens, or one halogen with one ester or nitro- or aldehyde or ketone group.

II. *Difference*, 10—20°.—This group includes alkyl + carboxyl or ketone, and alkyloxy- + alcohol, ester, aldehyde, ketone, or nitro-.

III. *Difference*, 20—80°.—Abnormal compounds. These are: alkyl + dialkylamino-, dialkylamido-, or nitro-; alkyloxy- + amino- or hydroxyl; halogen + alkylamino-, dialkylamino-, acylamino-, and hydroxyl; amino-esters and hydroxy-esters; all derivatives containing an amino- or hydroxy-group with any substituent other than alkyl.

TABLE II.

Summary.

	Alkyl.	CN.	O·Acyl.	SH.	C_nH_{2n}·OH.	C_nH_{2n}·NH_2.	O·Alk.	Halogen.	CO_2H.	CO_2Alk.	CHO.	CO·Alk.	COCl.	NHAlk.	NH·Acyl, etc.	NH_2.	$NAlk_2$.	CO·$NAlk_2$.	NO_2.	Aryl.	OH.
Alkyl	5·6	6·0	6·5	2·0	6·0	4·0	7·3	6·3	15·0	6·0	5·0	15·5	—	3·4	9·3	5·2	**27·0**	**37·0**	**20·3**	—	6·0
CN	6·0	—	—	—	—	—	6·0	17·5	—	—	—	—	—	—	—	—	—	—	—	—	—
OAcyl.........	6·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SH	2·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
C_nH_{2n}·OH ...	6·0	—	—	—	—	—	12·8	7·0	—	—	—	—	—	—	—	—	—	—	—	—	—
$C_nH_{2n}NH_2$ ...	4·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
OAlk.	7·3	6·0	—	—	12·8	—	6·5	7·6	—	16·0	14·5	12·3	—	—	—	**33·0**	—	—	13·5	—	**34·5**
Halogen ...	6·3	17·5	—	—	7·0	—	7·6	5·2	—	7·5	7·5	—	16·0	**24·0**	**25·0**	13·0	**26·0**	—	4·0	13·5	**43·5**
CO_2H	15·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CO_2·Alk.......	6·0	—	—	—	—	—	16·0	7·5	—	9·0	—	—	—	—	—	**30·0**	—	—	—	—	**33·0**
CHO	5·0	—	—	—	—	—	14·5	7·5	—	—	—	—	—	—	—	—	—	—	—	—	**43·0**
CO·Alk.	15·5	—	—	—	—	—	12·3	—	—	—	—	—	—	—	—	—	—	—	**20·0**	—	—
COCl	—	—	—	—	—	—	—	16·0	—	—	—	—	**23·0**	—	—	—	—	—	—	—	—
NHAlk.	3·4	—	—	—	—	—	—	**24·0**	—	—	—	—	—	**29·0**	**26·0**	—	—	—	—	—	—
NHAcyl ...	9·3	—	—	—	—	—	—	**25·0**	—	—	—	—	—	—	—	—	—	—	—	—	—
NH_2	5·2	—	—	—	—	—	**33·0**	13·0	—	**30·0**	—	—	—	**26·0**	**26·0**	—	—	—	—	**48·0**	—
$NAlk_2$	**27·0**	—	—	—	—	—	—	**26·0**	—	—	—	—	—	—	—	**50·0**	—	—	—	—	—
CO·$NAlk_2$ ...	**37·0**	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NO_2	**20·3**	—	—	—	—	—	13·5	4·0	—	—	—	**20·0**	—	—	—	—	—	—	19·0	—	**80·0**
Aryl	—	—	—	—	—	—	—	13·5	—	—	—	—	—	—	**48·0**	—	—	—	—	—	**33·0**
OH	6·0	—	—	—	—	—	**34·5**	**43·5**	—	**33·0**	**43·0**	—	—	—	—	—	—	—	**80·0**	**33·0**	**34·0**
Means :	10·2	9·8	6·5	2·0	8·6	4·0	14·9	16·2	15·0	16·9	17·5	19·3	19·5	18·1	17·2	22·2	34·7	37·0	26·1	31·5	39·1

It is to be noticed that the abnormality of the hydroxy- and amino-derivatives does not extend to those in which these groups are attached to a side-chain, as in the aromatic alcohols and benzylamine compounds; also, whilst a halogen, amino-, or hydroxy- with an *alkyl* group gives a normal compound, the analogous compounds with an *aryl* group instead of an alkyl (diphenyl derivatives) are, so far as they are known, highly abnormal.

The general impression conveyed by these results is that the property is not an additive one for the two substituents, but rather that it depends on the interaction of the two. This is shown, for example, in the behaviour of the halogens and the nitro-group, which with themselves or one another give normal compounds, whereas in conjunction with other groups, especially in amines or phenols, they cause great abnormality.

When we come to the order of the boiling points of the ortho-, meta-, and para-compounds, it is clear that the discussion of the normal compounds, where the differences are small, requires data more exact than many of those on which the foregoing tables are based. Among the abnormal compounds, on the other hand, the differences are large enough for trustworthy conclusions to be drawn from them. The general conclusion is that in the abnormal group the ortho- have by far the lowest boiling points, and the meta- and para- do not differ greatly, but the meta- nearly always have rather lower boiling points than the para-. This relation is supported, so far as concerns the phenol derivatives, by the solubilities in water, where the meta- and para- in all instances hitherto examined give very similar curves, whilst that of the ortho- is quite different. It is particularly remarkable that the ortho-compound, with the highest vapour pressure, is the least soluble in water.

There are, however, some exceptions to these rules as to the boiling points.* COCl:COCl, b. p. *o*-, 281°, *m*-, 276°, *p*-, 259°. This is entirely anomalous. The high boiling point of the ortho-compound may be due to the substance having the ring formula, as has already been suggested on chemical grounds; but, if so, the equally high boiling point of the meta-derivative would seem to point to a ring structure for this as well; also in the compounds Br:CN and $NO_2:NO_2$ the ortho-compound has a much higher boiling point than the other two.

Comparing the meta- and para-isomerides, we find that the para- has the higher boiling point in all but twelve cases. Excluding one of these, in which the difference is only 1° and may be due to experimental error, all the other eleven without exception contain one or two amino- or substituted amino-groups ($CH_3:NMe_2$,

* These compounds are conveniently described by means of the two substituents alone.

$CH_3:NEt_2$, $CH_3\cdot O:NH_2$, $Cl:NMe_2$, $NMe_2:NMe_2$, and NH_2 with NH_2, NHMe, NHEt, NMe_2, and NEt_2). This indicates some constitutional peculiarity which needs explanation.

The measurements given in the following paper of the vapour pressures of substituted benzoic acids at 100° enable the conclusions to be extended to these classes of compounds. It will be seen that the vapour pressures of the toluic acids, which are slightly abnormal, having a difference of boiling point of 15·5°, vary in the ratio of 4·5:1. The chlorobenzoic acids have about the same ratio. In the nitrobenzoic acids the difference is distinctly larger (20:1), and in the hydroxybenzoic and hydroxytoluic acids it is enormous (1300:1 and 300:1). It thus appears that whilst the compounds $CH:CO_2H$ and $Cl:CO_2H$ are almost normal, $NO_2:CO_2H$ is markedly abnormal, and $OH:CO_2H$ more so than any other compound yet examined. It will also be noticed that in these last two groups the ortho-compound is always the most, and the para- the least, volatile.

Summary.

With regard to the influence of position on the boiling point, the derivatives of benzene may be divided into two classes, namely, normal and abnormal.

(1) The normal derivatives are those in which the influence is small, the difference of boiling point seldom exceeding 10° for any set of isomerides. In this class the substituents are, as a rule, of an unchangeable type, such as alkyl (not aryl), or alkyloxy-, or ester groups. When all but one of the substituents are alkyl groups, the compound is almost always normal.

(2) Abnormal derivatives are those in which the boiling points differ by more than 10°, usually from 20° to 80°, the boiling points of the meta- and para- being near to one another, whilst that of the ortho- is much lower. In these compounds the substituents are of a reactive character. If a substance contains two reactive groups and, say, an alkyl, a change in the relative positions of the two reactive groups has a large effect on the boiling point, but a change in the position of the alkyl has only a small one.

These relations extend to the solubilities in water, so far as they have been observed. Normal compounds show similar solubilities; in abnormal compounds, the solubilities are very different, and when one of the substituents is a hydroxyl, the ortho-compound (in spite of its higher vapour pressure) is far less soluble in water than the meta- and para-, the solubilities of which, like their boiling points, lie close together.

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XLIX.—*Volatility in Steam: Benzoic Acid and it Derivatives.*

By Nevil Vincent Sidgwick.

Considering the technical importance of steam distillation, it is remarkable that it has been the subject of comparatively few scientific investigations. The volatility or otherwise of an organic substance in steam is one of the most familiar properties in organic chemistry, but only in a small number of instances (see Naumann, *Ber.*, 1877, **10**, 1421, 1819, 2014, 2099; Naumann and Müller, *Ber.*, 1901, **34**, 224; Ryland, *Amer. Chem. J.*, 1899, **22**, 384; Charabot and Rocherolles, *Bull. Soc. chim.*, 1904, [iii], **34**, 533; Richmond, *Analyst*, 1908, **33**, 209, 305; 1917, **42**, 125, 133; Stein, *J. pr. Chem.*, 1913, [ii], **88**, 83) have any attempts been made to determine it quantitatively.

Partly on account of the general interest of this property, and partly with the view of extending the data given in the preceding paper as to the influence of position on volatility to substances which decompose below their boiling points, I have been led to examine this subject, and in this paper an apparatus is described by which the volatility in steam of a substance from its saturated aqueous solution can readily be determined with an accuracy of 1 or 2 per cent. with quite a small quantity of material, and the results obtained with benzoic acid and a series of its derivatives are discussed.

In the distillate obtained under these conditions, the weights of the components are in the ratio of the products of their molecular weights into their partial pressures in the vapour. When they are immiscible, these partial pressures will be the vapour pressures of the pure components at the temperature of the distillation, where the total pressure is one atmosphere.

If any two vapour-pressure curves are compared, it will practically always be found (invariably if the boiling points of the two substances lie far apart) that as the temperature rises the ratio of the pressures approaches unity. Thus for ether and water the ratio at 0° is 40·4, and at 80° is 8·37; for benzoic acid and water it is 0·00220 at 100° and 0·0260 at 249°. The reason for this is easily seen. The change of vapour pressure with temperature is approximately given by the equation

$$\log p = A - \frac{B}{T},$$

where p is the vapour pressure at the absolute temperature T, and A and B are constants depending on the substance. For water in the neighbourhood of 100°, $A=8{\cdot}66$ and $B=2156$. For organic substances boiling above 100°, A varies within rather narrow limits, lying nearly always between 7·5 and 10, and usually between 8 and 9. The result is that if $\log p$ is plotted against $1/T$ for any number of substances, a series of straight lines is obtained radiating from points on the $\log p$ axis (where $1/T=0$, and hence $\log p=A$) which lie close together; that is, the lines all approach one another as the temperature rises. The distance between any two lines on this diagram, however, is equal to the difference of logarithms of the pressures of the two substances, that is, is the logarithm of the ratio of their vapour pressures. Hence, as the temperature rises, the value of $\log(p_1/p_2)$ approaches zero, and the ratio p_1/p_2 approaches unity.* It follows that in the process of steam distillation, where the object is always to get the maximum proportion of a substance of higher boiling point than water in the distillate, the fficiency is greater the higher the temperature or the greater the ressure at which the distillation is carried out. This fact has een recognised in technical practice, although the reason has not itherto been stated.

If the substance is perceptibly soluble, it will lower the vapour ressure of the water; the distillation will take place at a higher emperature, and the proportion of the substance in the distillate ill be increased. With most of the substances dealt with in this aper, the influence of this factor is small; it is also easily allowed or if the temperature of the liquid is known. In dealing with the ffect of solubility on the partial pressure of the other component, he substance A, two cases have to be distinguished, that in which is solid and that in which it forms a second liquid layer. If the ubstance is solid, its partial pressure in the vapour from the aturated solution is equal to the vapour of the solid substance at he temperature of the distillation. This method, in fact, offers he simplest means of measuring the vapour pressure of a solid at 00° down to values of the order of a thousandth of a mm. (or ven lower if sufficiently accurate analytical methods are available). 'or the purpose of comparison, however, it is more important to now the vapour pressure in the liquid than in the solid state. As as pointed out in discussing the solubilities of the toluic acids T., 1915, **107**, 1209), the regularities observed in liquid–liquid ystems disappear when the solid phase is formed, owing, no doubt,

* Charabot and Rocherolles (*loc. cit.*) laid down the rule that the ratio of rganic substance to water in the distillate always approaches unity as the mperature rises; but this is obviously not always true.

to the effect of the crystallographic forces, which is most clearly shown in the wide divergences in melting point of otherwise similar substances. The vapour pressure of a solid is necessarily less than that of the (supercooled) liquid at the same temperature, and the more so the further that temperature is removed from the melting point. The relation between the two can be calculated if the heat of fusion is known, for it can be shown that if p, p' are the vapour pressures of the substance in the liquid and solid states at a temperature T (absolute) below its melting point T_0, and if W is the molecular heat of fusion in calories, then

$$2{\cdot}3026 \log \frac{p}{p'} = \frac{W}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where $R = 1{\cdot}985$.

As an example of the influence of this factor, we may take p-toluic acid (m. p. 177°). Its heat of fusion is not exactly known, but it may be taken to be of the order of 5000 cals. per gram-molecule. At 100° we have

$$2{\cdot}3026 \log \frac{p}{p'} = \frac{5000}{1{\cdot}985}\left(\frac{1}{373} - \frac{1}{450}\right)$$

whence $\log p/p' = 0{\cdot}5019$ and $p/p' = 3{\cdot}17$. The observed vapour pressure of the solid acid at 100° is 0·216 mm. It follows that that of the liquid at 100° would be $0{\cdot}216 \times 3{\cdot}17 = 0{\cdot}685$ mm., which is very near to the values for the ortho- (0·970) and meta- (0·607) acids, which are liquid under water at 100°. These calculations are not worth discussing in more detail until the heats of fusion of the acids in question have been measured with greater accuracy, which is now being done.

When the substance forms a second liquid layer, the vapour pressure which is being measured is the partial pressure of the substance in the vapour in equilibrium with either of the two liquid phases (since the same vapour must be in equilibrium with both). If we consider the phase richer in A, it is obvious that p_A will be lowered by the presence of dissolved water. It will be less than the vapour pressure of pure liquid A, and also less than that of solid A. It is difficult to calculate how much it is diminished, because binary liquids in the neighbourhood of the point at which they separate into two liquid layers depart widely from the simple solution laws. It may, however, be pointed out that in the case, for example, of m-toluic acid (m. p. 110·5°; triple point with water 91·8°), the liquid at the triple point, where the partial pressure of the acid in the vapour is equal to the vapour of the solid acid, contains 44·2 molecules per cent. of water, whilst

at 100° the acid layer contains 49·8 molecules per cent. Assuming the vapour-pressure law, we should expect the extra 5·6 molecules per cent. of water to lower the vapour pressure of the acid by the same percentage, or less if the acid is associated in the liquid to a smaller degree than the water, and this may be taken as giving a rough idea of the magnitude of the effect. Young ("Fractional Distillation," 1903, p. 92) found that at atmospheric pressure the amount of aniline in the distillate from a mixture of aniline and water was 14 per cent. less than that calculated from the vapour pressures of the pure components, and at this temperature the aniline dissolves about 35 molecules per cent. of water. With benzoic acid the vapour pressure of the pure liquid has been measured by Kahlbaum (*Zeitsch. physikal. Chem.*, 1898, **26**, 603) down to 132·5°, where it is 10 mm. By extrapolation, using the logarithmic formula, it is found to be 1·67 mm. at 100°. Its heat of fusion is 4830 cals. (Ciamician and Garelli, *Zeitsch. physikal. Chem.*, 1895, **18**, 54), and its melting point 122·7°. Hence the vapour pressure of the solid acid at 100° is 1·15 mm. As the triple point is only 5° lower, we should not expect the partial pressure of the acid in the vapour at 100° to be much lower than that of the solid acid at the same temperature. It was actually found by the steam distillation method to be 1·129 mm., a difference of only 2 per cent.

EXPERIMENTAL.

A series of preliminary experiments with a pure sample of benzoic acid showed that the steam became saturated with the acid when it had passed through two small flasks containing a mixture of the acid and water, but that it was essential to avoid recondensation of the vapour after it had left the liquid, as this always gave low results, owing no doubt to the fact that the volatility is less at lower temperatures. The form of apparatus finally adopted was as follows. The acid was contained in two 120 c.c. flasks with short, wide necks. Steam from a boiler was passed through a trap to catch water-drops, and was led to the bottom of the first flask and thence by a short bent tube to the bottom of the second. From this it passed through a Kjeldahl trap to the condenser. The cork of the second flask carried a thermometer graduated in fifths of a degree, with its bulb reaching nearly to the bottom of the flask. The flasks were immersed up to their necks in a glycerol-bath, which was kept a few degrees above the temperature of the distillation, and the whole of the apparatus above the glycerol was carefully lagged—the tube from the steam-trap to the first flask and that connecting the two flasks being wrapped in felt, and

the Kjeldahl-trap surrounded by a jacket moulded on to it from asbestos millboard and dried. This was cut into two halves, so that it could be removed for cleaning the trap. The amount of acid in each flask was from 3 to 20 grams (according to the solubility), and the steam was passed at a rate of 2—4 grams per minute. With this apparatus it was found that, although the first fraction of the distillate gave a low value, subsequent fractions were of constant composition, as is shown by the following two experiments (the successive fractions were from 70 to 150 c.c. each; the numbers give the percentage of acid in the distillate): Expt. I: 0·90, 1·004, 0·994, 0·980, 0·984. Expt. II: 0·89, 1·004, 0·981, 1·000, 1·018.

The results obtained on any one day were found to agree better among themselves than the means of different days did with one another. This was traced to changes in the barometric pressure. From Kahlbaum's measurements (*loc. cit.*) of the vapour pressure of benzoic acid, R, the ratio of its vapour pressure to that of water can be calculated at a series of temperatures in the neighbourhood of 100°. It is found that R increases for 1° rise of temperature by 2·76 per cent., or, since an increase of pressure of 27·4 mm. raises the boiling point of water by 1°, 1 mm. rise of the barometer will increase the proportion of acid in the distillate by 0·101 per cent. of its value, which is quite an appreciable amount. The following table shows the results obtained when this correction is applied. The four experiments were carried out on different days. The value given for the percentage of acid in the distillate is in each case the mean of the titrations of from three to six different fractions. The numbers under "correction" are the amounts which must be added to give the true composition of the distillate under 760 mm. pressure.

Expt.	Pressure.	Weight-percentage of acid in distillate.	Correction.	Corrected percentage.
D	745·0	0·987	+0·015	1·002
E	750·2	0·991	+0·010	1·001
F	750·2	0·999	+0·010	1·009
G	755·5	1·006	+0·004	1·010
			Mean......	1·006

To prove that the vapour was saturated with acid, the distillation was repeated under the same conditions, except that the steam was not generated from water alone, but from a mixture of 800 c.c. of water and 80 grams of pure benzoic acid. In this way, saturation must be attained. It was difficult to secure a steady flow of steam, as the two layers in the flask made the liquid boil irregularly, and this might be expected to give a slightly low value, as any

interruption of the distillation leads to some re-condensation of the vapour. The mean value so obtained was 0·984 per cent. at 750·4 mm., corresponding with 0·994 at 760 mm. This is 1·2 per cent. below the mean of the other four experiments, which are doubtless more trustworthy, for the reason mentioned, but it is enough to show that the apparatus secures complete equilibrium between the solution and the vapour.

With the other acids examined, the measurements were made in less detail, and only the final means are quoted; these are always the means of the concordant titrations of at least three different fractions of distillate. The accuracy naturally varies with the nature of the acid. When this melts under water below 100° there is little difficulty. When it remains solid, it is not easy to remove it completely from the condenser, although this can generally be done by running out the water. It may be assumed that the mean results are within 2 or 3 per cent. of the truth in all cases, except where (as with *p*-hydroxybenzoic acid) the amount of acid in the distillate is too small for accurate titration.

The acids used were in most instances laboratory specimens purified by recrystallisation. I am greatly indebted to Miss E. Ewbank for her kind assistance in the preparation of some of these acids and in the purification of others.

The preparation and behaviour of the individual acids may be briefly described as follows. (Acids marked with an asterisk are liquid under water at 100°.) The solubility data, where no other reference is given, are derived partly from unpublished measurements made by Miss Ewbank in this laboratory and partly from the work of Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien.*, 1909, **118**, II*b*, 695). The solubilities are expressed in grams of acid in 100 grams of solution.

Benzoic Acid.*—A specially pure sample free from chlorine: purified by recrystallisation. M. p. 122·7°. Triple point with water, 95°. Solubility in water at 100°, 8·0 per cent. (Alexéev, *Ann. Phys. Chem.*, 1888, [iii], **28, 305.)

**Phenylacetic Acid.*—Pure laboratory specimen. M. p. 76·7°. Triple point, 46·5°. Solubility at 100°, 11·2 per cent.

**β-Phenylpropionic Acid.*—Recrystallised from light petroleum. M. p. 48·6°. Triple point, 34·0°. Solubility at 100°, 3·5 per cent.

Toluic Acids.†—Recrystallised from water.

	M. p.	Triple point.	Solubility.
*Ortho	102·4°	93·5°	2·97 per cent.
*Meta	110·5	91·8	1·98 ,,
Para	176·8	(142·0)	1·16 ,,

† Solubility data: Sidgwick, Spurrell and Davies, T., 1915, **107**, 1207. I take this opportunity of expressing my regret that when this paper was

Hydroxybenzoic Acids.—Recrystallised from water until their melting points and solubilities in water were not further changed. All these acids remain solid. The value given in the table for the volatility of the para-acid is only approximate. One drop of $N/10$-alkali was more than sufficient to neutralise the acid in 100 c.c. of distillate, and as the acid cannot be sharply titrated, it did not seem worth while to use $N/100$-alkali.

	M. p.	Solubility at 100°.
Ortho	159·0°	6·45 per cent.
Meta	201·3	36·9 „
Para	213·0	33·5 „

Hydroxytoluic Acids.—The acids $CH_3:CO_2H:OH = 1:3:2$, $1:4:3$, and $1:3:4$ were obtained from the technical cresotic acids by distillation in steam and recrystallisation. The $1:3:6$-acid was boiled with animal charcoal and recrystallised from alcohol and water. The $1:4:2$-acid was prepared by the sulphonation of *p*-toluic acid and fusion of the product with alkali (Perkin and Meldrum, T., 1908, **93**, 1419). It was purified by recrystallisation from water.

$CO_2H:OH:CH_3$.*	M p.	Triple point.	Solubility at 100°.
1 : 2 : 3	167·0°	(129·0°)	1·16 per cent.
1 : 2 : 4	177·8	(131·0)	0·94 „
1 : 2 : 5	152·5	(107·8)	2·15 „
1 : 3 : 4	172·4	—	4·36 „
1 : 4 : 3	207·0	—	5·25 „

Nitrobenzoic Acids.—The ortho-acid was purified through the barium salt (Holleman, *Rec. trav. chim.*, 1898, **17**, 247). The behaviour of this acid was quite peculiar. It gives with water an unbroken solubility curve up to its melting point without a two-liquid portion. This curve, like that of salicylic acid, is very flat in the middle, that is, the solubility increases very greatly for a small rise of temperature. For example, at 78° it is 20 per cent. and at 82° it is 70 per cent. In the distillation, it was found impossible to get the acid to remain solid in the presence of steam. It melted at once, forming a homogeneous liquid. Its temperature varied with that of the glycerol-bath, remaining some 8—12° below it. Finally, a series of fractions were taken at 117° (bath, 123—126°), which gave concordant titrations.

The most probable explanation of this behaviour (which was not observed with any other acid) is that the vapour-pressure curve of

published we were unaware of the paper by Flaschner and Rankin quoted above, in which the solubilities of the toluic acids in water are given. Our results are in substantial agreement with theirs.

* The substituents are arranged in the order of their influence on the volatility.

the saturated solution (which with any substance giving an unbroken solubility curve must rise with the temperature to a maximum and then fall to the vapour pressure of the pure substance at its melting point) never attains the value of one atmosphere. If so, the solution which the acid forms in contact with steam at one atmosphere, since it must have a vapour pressure of 760 mm., must be somewhat unsaturated, and both the composition of this solution and the partial pressure of the acid will vary with the temperature.

The meta- and para-acids were purified by recrystallisation.

	M. p.	Triple point.	Solubility at 100°.
Ortho	146·8°	—	92·8 (at 117°)
*Meta	141·4	76·8°	10·5
Para	242·4	—	0·29

Chlorobenzoic Acids.—The ortho- and para-acids were prepared from the corresponding toluidines by Sandmeyer's reaction and purified by recrystallisation. The meta-acid was recrystallised from benzene.

	M. p.	Triple point.	Solubility at 100°.
Ortho	140·3°	(104·8°)	4·02 per cent.
Meta	154·5	(123·8)	0·5 ,,
Para	241·5	—	0·11 ,,

Determination of Temperature.—This was somewhat inaccurate, owing to the uncertain correction for the emergent stem, which was determined by conducting a distillation with nothing but water in the bulbs and varying the temperature of the bath. In the actual distillation of the acids, the thermometer readings remained steady in nearly every case to about 0·04°, but with most acids the elevation of the boiling point is so small that the readings are of no great value; they are therefore only quoted when they amount to 0·1° or more.

The results are collected in the following table. The first column gives the name of the acid; the second (dt) the elevation of the temperature above 100° (reduced to 760 mm.); the third the percentage by weight of the acid in the distillate; the fourth the partial pressure of the acid in hundredths of a mm. The latter is calculated from the formula

$$p_A = \frac{\text{Wt. of acid}}{\text{Wt. of water}} \times \frac{760 \times 18}{M},$$

where M is the molecular weight of the acid. The fifth column gives the solubility (in grams per 100 grams of solution) of the acid in water at the temperature of the distillation. The sixth gives the partition-coefficient of the acid between the vapour and

Acid.	dt.	Percentage in distillate.	Vapour pressure in mm. × 100.	Solubility.	Partition coefficient × 10⁶.	Relative Vapour pressure	Relative Partition.
Benzoic*	0·12°	1·006	112·9	8·0	73·9	1·0	1·0
Phenylacetic*	0·16	0·294	29·55	11·2	15·43	0·262	0·208
β-Phenylpropionic *	—	0·247	22·5	3·5	41·4	0·200	0·560
Toluic: ortho*	0·10°	0·964	97·0	2·97	191·0	4·49	1·75
meta*	—	0·604	60·7	1·98	136·0	2·81	1·25
para	—	0·215	21·6	1·16	108·9	1·0	1·0
Hydroxybenzoic: ortho	—	0·400	39·7	6·45	36·5	1320·0	6890·0
meta	1·06°	0·0015	0·149	36·9	0·024	5·0	4·53
para	0·91	0·0003	0·030	33·5	0·005	1·0	1·0
Hydroxytoluic:							
CO_2H : OH : CH_3 ortho : 3	—	0·261	23·5	1·16	132·4	326·4	1471·0
,, : 4	—	0·135	12·1	0·94	80·1	168·0	890·0
,, : 5	—	0·202	18·2	2·15	55·3	253·0	614·0
meta : 4	—	0·0196	1·76	4·36	2·64	24·4	29·3
para : 3	0·17°	0·0008	0·072	5·25	0·090	1·0	1·0
Nitrobenzoic: ortho	17·0°	0·0246	2·01	92·8	0·156	20·9	0·0655
meta*	0·10	0·0085	0·70	10·5	0·479	7·29	0·201
para	—	0·0017	0·096	0·29	2·38	1·0	1·0
Chlorobenzoic: ortho	—	0·206	18·03	4·02	30·2	4·01	0·110
meta	0·63°	0·225	19·70	0·5	260·0	4·38	0·96
para	—	0·0515	4·50	0·11	275·0	1·0	1·0

the liquid, that is, the concentration in the vapour divided by that in the saturated solution. The last two columns give the values of the vapour pressures and the partition-coefficients referred to those of the para-acid (or with the first three acids to those of benzoic acid) as unity.

Volatility and Boiling Point.

To bring these results into line with the data tabulated in the preceding paper, it would be necessary to calculate the boiling points of the acids from their vapour pressures at 100°. This can be done if we assume a value for either of the two constants A and B of the vapour-pressure formula. Such an assumption, however, is scarcely justified; where the vapour pressures are abnormal we may expect these constants to be abnormal also, but experience shows that heats of evaporation do not vary very widely, and hence a large difference in the vapour pressure at 100° may be taken to involve a large difference in boiling point.

It is more satisfactory to take as the basis of comparison the ratio of the vapour pressures of the isomerides at 100°. These values can be obtained by interpolation for those derivatives the vapour-pressure curves of which have been measured over a suitable range of temperature, and the ratios compared with those given by the substituted benzoic acids. The following table is constructed in this way. The values are relative, that for the para- (or, where that is missing, the meta-) isomeride being taken as unity. The last column gives the greatest difference in boiling

	Relative vapour pressure at 100°.			Greatest difference in b. p.
Substituents.	Ortho.	Meta.	Para.	
[1]$CH_3 : CH_3$	0·788	0·862	1	5·6°
[2]$CH_3 : Cl$	1·097	0·896	1	3·0
[3]$CH_3 : NH_2$	1·037	0·870	1	3·6
[3]$CH_3 : OH$	1·722	1·026	1	11·0
[3]$CH_3 : NO_2$	1·653	—	1	17·3
[3]$Cl : NH_2$	2·277	1·0	—	19·7
$CH_3 : CO_2H$	4·49	2·81	1	15·5
$Cl : CO_2H$	4·01	4·38	1	—
$NO_2 : CO_2H$	20·9	7·3	1	—
$OH : CO_2H$	13 20·0	5·0	1	—
$CO_2H : OH : CH_3$	1 : 2 : 3 326·0	—	—	—
	1 : 2 : 4 168·0	1 : 3 : 4 24·4	1 : 4 : 3 1	—
	1 : 2 : 5 253·0	—	—	—

[1] Woringer, *Zeitsch. physikal. Chem.*, 1900, **34**, 262.
[2] Feitler, *ibid.*, 1889, **4**, 71.
[3] Kahlbaum, *ibid.*, 1898, **26**, 603.

point at 760 mm. The first three series show the behaviour of normal compounds, in the sense in which this term is used in the preceding paper; the cresols are slightly, and the last two series distinctly, abnormal. Of the acids dealt with in the present paper, the boiling points of the toluic acids only have been determined.

The vapour-pressure curves from which the data for the first six series are obtained are all, of course, those of liquids. The differences among the acids might no doubt be somewhat reduced if they were compared in the liquid state, account being taken of the difference of vapour pressure of solid and liquid at temperatures some way below the melting points; as we have seen, the ratio for the toluic acids is reduced in this way to 1·6. The extreme abnormality of the hydroxy-derivatives is very marked.

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L.—*Observations on Some Organic Compounds of Arsenic.*

By Alex. McKenzie and John Kerfoot Wood.

The following is an account of part of the work carried out in Dundee during 1918 in connexion with the Chemical Warfare Department of the Ministry of Munitions. It is published with the consent of the General Staff of the War Office.

Ethoxydichloroarsine.

When molecular quantities of sodium ethoxide and arsenic trichloride were employed, the action could be regulated so as to proceed according to the equation

$$NaOEt + AsCl_3 = NaCl + EtO{\cdot}AsCl_2.$$

A solution of 15 grams of sodium (1 atom) in 300 c.c. of ethyl alcohol was gradually added, within an interval of two and a-half hours, to 118 grams of commercial arsenic trichloride (1 mol.). The mixture was kept cool by immersion in cold water, and was shaken after each addition of the ethoxide. The product was then heated for one hour longer, the sodium chloride separated, and the excess of alcohol removed.

Ethoxydichloroarsine, $EtO{\cdot}AsCl_2$, is a colourless liquid which boils at 145—146°/751 mm., whereas arsenic trichloride, according

to Thorpe, boils at 130·2°/760 mm. The yield amounted to 70 grams, which is 59 per cent. of the theoretical.

Found: As=39·04. Cl=37·2.

$C_2H_5OCl_2As$ requires As=39·27; Cl=37·1 per cent.

Ethoxydichloroarsine fumes on exposure to air. When poured into cold water, a copious precipitate of arsenious oxide is immediately formed.

Diethoxychloroarsine.

It is also possible to regulate the action of sodium ethoxide on arsenic trichloride, so that two ethoxy-groups are introduced into the molecule of the latter.

A solution of 30 grams of sodium (2 atoms) in 600 c.c. of ethyl alcohol was added slowly to 118 grams of arsenic trichloride (1 mol.). The addition of the ethoxide lasted two and a-half hours. After twenty-four hours at the ordinary temperature, the mixture was heated for one hour, the sodium chloride separated, and the excess of alcohol removed. The residual liquid was distilled under diminished pressure.

Diethoxychloroarsine, $(OEt)_2AsCl$, is a colourless liquid, which boils at 64—65°/20 mm. and at 159—160°/760 mm.

The yield was 90 grams, which is 69 per cent. of the theoretical.

Found: As=37·6. Cl=17·3.

$C_4H_{10}O_2ClAs$ requires As=37·4; Cl=17·7 per cent.

The behaviour towards water is similar to that of ethoxydichloroarsine.

Ethyldichloroarsine.

Ethyldichloroarsine was obtained by La Coste (*Annalen*, 1881, **208**, 33) by the action of arsenic trichloride on mercury diethyl:

$$AsCl_3 + HgEt_2 = AsEtCl_2 + HgEtCl.$$

This method was obviously unsuitable for the preparation in quantity of this compound. The following method gave a satisfactory result.

Auger (*Compt. rend.*, 1903, **137**, 925) having shown that sulphur dioxide reduces sodium methylarsinate to methylarsenious oxide, the reduction of magnesium ethylarsinate (Dehn, *Amer. Chem. J.*, 1905, **33**, 132) was conducted in the following manner. Thirty-four grams of the salt were added to 250 c.c. of water, 10 grams of iodine added, and a current of sulphur dioxide was passed into the solution for four and a-half hours. The clear solution gradually became turbid, owing to the separation of a canary-

yellow precipitate. This would indicate that the ethylarsinic acid had been reduced to ethylarsenious oxide, $EtAsO$, which, with hydrogen iodide, formed ethyldi-iodoarsine, $EtAsI_2$.

We found, however, that the preparation of the magnesium salt was unnecessary as a preliminary stage for the isolation of ethyl-di-iodoarsine, as the latter compound could be prepared directly in the following manner.

Arsenious oxide (159 grams) was dissolved in a solution of sodium hydroxide (193 grams) in 500 c.c. of water. The solution was poured into 1400 c.c. of water, ethyl iodide (250 grams) added, and then sufficient rectified spirit to form one phase. The mixture remained at the temperature of the laboratory for six days. After removal of the bulk of the alcohol, the residual liquid (1300 c.c.) was acidified with concentrated hydrochloric acid, the precipitate removed, and a current of sulphur dioxide passed into the filtrate. The colour of the iodine quickly disappeared, and the yellow ethyl di-iodoarsine began to separate as an oil. The sulphur dioxide was passed for about three and a-half hours, 330 c.c. of concentrated hydrochloric acid being added at intervals. The oil was separated from the liquid. In this case there was no solid present; but in other preparations, where the original concentration of the mixture resulting from Meyer's reaction had been carried further than in the present case, a mixture of solid and oil resulted. It is convenient to adjust the concentration so that only oil separates. From the yellow, aqueous liquid a small additional amount of oil was obtained by the further addition of hydrochloric acid and sulphur dioxide. The yield of ethyldi-iodoarsine was 272 grams.

For the conversion of this quantity of ethyldi-iodoarsine into ethylarsenious oxide, the oil was dissolved in 750 c.c. of benzene and a mixture of 60 grams of calcium chloride and 192 grams of anhydrous sodium carbonate added. After the mixture had been heated on the water-bath for two hours, the yellow colour disappeared. The solution was poured off, and the residual solid extracted with benzene. The benzene was distilled from the solution, and the resulting oil heated until its temperature was about 120°. The yield of ethylarsenious oxide was 100 grams.

For the conversion of the oxide into ethyldichloroarsine according to the equation

$$EtAsO + 2HCl = EtAsCl_2 + H_2O,$$

100 grams were placed in a separating funnel, and 25 c.c. of concentrated hydrochloric acid were added. The funnel was then surrounded with cold water, and a current of hydrogen chloride passed through the oil for about three hours, the completion of the reaction being shown by the escape of hydrogen chloride by

the exit tube. The oil was separated, dried with calcium chloride. freed as far as possible from hydrogen chloride by means of a current of carbon dioxide, and distilled. Twenty-nine grams of a fraction of lower boiling point, containing a considerable proportion of ethyldichloroarsine, were first collected. The product boiling between 150° and 155° amounted to 101 grams. The compound can be obtained quite pure by fractionating further.

In connexion with the preparation of ethyldichloroarsine in quantity, the following points which emerge from the preceding description are worthy of notice: (1) Sodium hydroxide may be used in place of the more expensive potassium hydroxide in Meyer's reaction. (2) The separation of magnesium ethylarsinate is unnecessary. (3) The sodium iodide formed in the first reaction is utilised, and no further addition of the expensive potassium iodide is required, as is the case if the magnesium salt is first isolated and then reduced. (4) There is a considerable saving of time.

The following are the details of the yields in several of the preparations:

Ethyl iodide. Grams.	Ethylarsenious oxide. Grams.	Ethyldichloroarsine. Grams.
250	100	101
	85	87
	92	89
	93	99
	95	97
	100	107
	99	
	111	
	109	
	93	
500	178	

The yield of ethyldichloroarsine is really better than is repre-ented above, since a fair quantity can be recovered from the istillates of lower boiling point on fractionation. The yield of thylarsenious oxide is more than 50 per cent., calculating on the thyl iodide initially used; the yield calculated from the ethyl odide actually entering into reaction is very much greater, since a onsiderable quantity of ethyl iodide can be recovered. The yield f ethyldichloroarsine from ethylarsenious oxide is more than 0 per cent. of the theoretical.

It was thus clear that the yield would probably be improved by levating the temperature at which the first stage (Meyer's reaction) took place. Experiments were begun to substitute ethyl hloride for the more expensive ethyl iodide, but the work was topped at this point, when the conclusion was reached that it

would be necessary to carry out the reaction with ethyl chloride under pressure.

Phenylethoxychloroarsine.

This compound was prepared according to the equation

$$PhAsCl_2 + NaOEt = NaCl + PhAsCl \cdot OEt.$$

4·6 Grams of sodium (1 atom) were dissolved in 100 c.c. of ethyl alcohol, and the solution was gradually added to 44·6 grams of phenyldichloroarsine (1 mol.) during half an hour. The mixture was then heated on the water-bath for two and a-half hours, cooled, the sodium chloride and then the alcohol removed, and the residue distilled under diminished pressure.

Phenylethoxychloroarsine, $PhAsCl \cdot OEt$, is a colourless oil which boils at 125—126°/12 mm. The yield was 37 grams, or 80 per cent. of the theoretical.

Found: Cl = 15·1.

$C_8H_{10}OClAs$ requires Cl = 15·2 per cent.

It gradually undergoes hydrolysis when kept in contact with water, being transformed into a white solid, which, when crystallised from petroleum (b. p. 90—105°), separates in needles melting at 127—130°. It is curious that this product has a melting point considerably higher than that recorded in the literature for phenylarsenious oxide.

Formation of Unstable Cyano-compounds.

Evidence was obtained that the following compounds are very unstable, owing to the ease with which they underwent hydrolysis: phenylchlorocyanoarsine, phenyldicyanoarsine, and ethyldicyanoarsine. It was not found possible to isolate them.

Action of Hydrogen Cyanide on Diphenylethoxyarsine: Diphenylcyanoarsine.

Diphenylchloroarsine was treated with sodium ethoxide,

$$Ph_2AsCl + NaOEt = Ph_2As \cdot OEt + NaCl,$$

the resulting ethoxy-compound being then acted on by hydrogen cyanide,

$$Ph_2As \cdot OEt + HCN = Ph_2As \cdot CN + EtOH.$$

2·3 Grams of sodium (1 atom) were dissolved in 100 c.c. of ethyl alcohol, and the solution was added to 26 grams of pure diphenylchloroarsine (1 mol.) dissolved in 50 c.c. of ethyl alcohol. The addition lasted one hour. After the mixture had been heated for one hour on the water-bath, the sodium chloride and the alcohol

were removed. The residue was a viscid oil, which solidified partly when kept overnight. It was then heated at 140° for three hours in a current of dry hydrogen cyanide. On cooling, the oil was washed with water, and a nucleus of the solid form of diphenylcyanoarsine, prepared by the method described later, was added; this caused the oil to crystallise. The product was washed with light petroleum and dried under diminished pressure. Twenty grams of a solid melting at 30—34° were obtained, and this corresponds with an 80 per cent. yield of diphenylcyanoarsine.

Action of Hydrogen Cyanide on Diphenylarsenious Oxide.

Diphenylcyanoarsine was next prepared by converting diphenylchloroarsine into diphenylarsenious oxide, which was then acted on by hydrogen cyanide:

$$2Ph_2AsCl + 2NaOH = H_2O + 2NaCl + Ph_2As{\cdot}O{\cdot}AsPh_2,$$
$$Ph_2As{\cdot}O{\cdot}AsPh_2 + 2HCN = 2Ph_2As{\cdot}CN + H_2O.$$

The product obtained by the action of gaseous hydrogen cyanide on molten diphenylarsenious oxide was distilled under diminished pressure.

Diphenylcyanoarsine boils at 213°/21 mm. (Found: N=5·4. $C_{13}H_{10}NAs$ requires N=5·5 per cent.).

From 25 grams of diphenylarsenious oxide, yields of 23 and 24 grams, respectively, of the pure, redistilled oil were obtained in successive experiments, corresponding with a yield of about 90 per cent. of the theoretical.

A most important property of this compound is the fact that it is sensitive to alkali in a remarkable degree. This was first noticed when a thin film of the oil, prepared as just described, was left exposed to the atmosphere in a crystallising dish at the ordinary temperature. The film was gradually converted into a solid, and it appeared that the oily diphenylcyanoarsine had crystallised. On examining the solid, it was found, however, that it consisted of diphenylarsenious oxide, as a determination of the melting point both alone and in presence of some of the oxide showed. It was proved that the result was not due to the presence of unattacked diphenylarsenious oxide in the original oil, and the inference was that the conversion of the oily cyano-compound into the oxide had been effected catalytically by the alkali of the glass vessel. It was next found that the oil solidified fairly quickly when kept in contact with *N*/10-aqueous sodium hydroxide at the ordinary temperature, and very quickly when warmed with alkali of this strength. A portion of the solid obtained in this manner was crystallised

from light petroleum, and a determination of its melting point showed that it consisted of diphenylarsenious oxide.

This interesting change may occur in the following stages:

$$Ph_2As\cdot CN + H_2O = Ph_2As(CN)<^{H}_{OH},$$

$$Ph_2As(CN)<^{H}_{OH} = Ph_2As\cdot OH + HCN,$$

$$2Ph_2As\cdot OH = H_2O + Ph_2As\cdot O\cdot AsPh_2.$$

The solid modification of diphenylcyanoarsine was obtained in the following manner. The crude oil resulting from the action of hydrogen cyanide on diphenylarsenious oxide was washed twice with water, and left in contact with solid calcium chloride overnight. It was then found to consist of a solid and very little oil. A portion of the solid was then washed with light petroleum, and found to melt at about 31—32° (Sturniolo and Bellinzoni, *Gazzetta*, 1919, **49**, ii, 326, give 35°). A nucleus added to some of the pure oil caused the latter to crystallise immediately.

According to La Coste and Michaelis (*Annalen*, 1880, **201**, 222), diphenylchloroarsine is only sparingly soluble in sodium hydroxide or potassium hydroxide on heating. The mobility of the halogen in diphenylchloroarsine is, however, much greater than would be inferred from the data in the literature; the chlorine can be displaced very easily under the following conditions, and the method now described is a convenient one for the preparation of diphenylarsenious oxide in quantity.

Sodium hydroxide (325 grams) was dissolved in water (1500 c.c.), and, when the temperature of the solution had fallen to 50°, diphenylchloroarsine (500 grams) was added. The solid melted, and the temperature was then gradually raised to 70° within fifteen minutes, during which time the mixture was stirred vigorously. When once the oil began to harden, it was transformed in the course of a few minutes into a hard solid. The temperature was maintained at 70° for fifteen minutes longer, with occasional stirring, and, when cold, the liquid was decanted from the solid, which was then powdered and thoroughly washed with water until the washings were free both from alkali and chloride. The oxide was then collected and dried on porous plates. If kept at the ordinary temperature, the product at this stage becomes constant in weight very slowly. It was found practical to dry in air for a day at the ordinary temperature, and then at 60° to 70° until the weight was constant. The yield of anhydrous oxide was 435 grams, which is 97 per cent. of the theoretical. When crystallised from light petroleum, the oxide melts at 92·5—93·5°, whereas La Coste and Michaelis (*loc. cit.*) give 91—92°.

The action took place in accordance with the equation

$$2Ph_2AsCl + 2NaOH = 2NaCl + H_2O + Ph_2As{\cdot}O{\cdot}AsPh_2.$$

In the majority of our experiments on the preparation of diphenylcyanoarsine, 150 grams of diphenylarsenious oxide were used each time. The flask containing this was placed in a bath of fusible metal, the temperature of which was gradually raised from 120° to 160°. Dry hydrogen cyanide was passed for about five hours through the molten diphenylarsenious oxide. The contents of the flask were allowed to cool, and, while still slightly warm, were poured into a porcelain dish, when solidification took place gradually. The yield of uncrystallised product was practically theoretical. If it is desired to keep the product for any length of time, it should be dried under diminished pressure until constant in weight.

It was also found that diphenylcyanoarsine can be obtained by allowing diphenylarsenious oxide to remain in contact with a concentrated aqueous solution of hydrogen cyanide at the ordinary temperature. The action of anhydrous hydrogen cyanide on diphenylarsenious oxide at the ordinary temperature would, in our opinion, be the most convenient method of preparing this compound on the large scale, especially if it is desired to obtain a product which will be fairly stable on keeping.

Our first experiment on the preparation of diphenylcyanoarsine was made with diphenylchloroarsine and potassium cyanide, but, as the ease with which the compound was hydrolysed was recognised at an early stage, the use of an aqueous solution of potassium cyanide was purposely avoided, as we were convinced that the method would be unsuitable for the preparation of the compound in a state of purity. The following experiment, carried out at a later stage with rectified spirit as the solvent, may, however, be quoted in this connexion. A mixture of 133 grams of diphenylchloroarsine and 50 grams of potassium cyanide was gently heated under reflux for five hours with 250 c.c. of rectified spirit. The liquid gradually darkened, and ultimately became red. It was left overnight, and the solid was removed. The filtrate separated into two layers. To the lower layer (47 grams), a nucleus of the solid diphenylcyanoarsine was added, and crystallisation began slowly. After one day in the ice-chest, the crystalline deposit amounted to 18 grams; when washed with ether, it melted at 32–34°. The upper layer was mixed with an excess of water. The resulting oil (61 grams) was removed, the aqueous solution being extracted with ether, and the ethereal solution added to the oil. To this ethereal solution were also added the ethereal washings from the 18 grams. The ethereal solution was dried with

sodium sulphate, the ether distilled, the residue mixed with the liquid portion of the original lower layer, and the whole heated at 140—150° to remove all the ether and alcohol. After a fort-night in the ice-chest, 50 grams of solid and 47 grams of liquid were present. The total yield of solid cyano-compound was 68 grams, and of solid plus liquid 115 grams.

It is certain that, when aqueous potassium cyanide is used, some of the diphenylchloroarsine will be converted into diphenyl-arsenious oxide, owing to the alkalinity of the liquid, and it is equally certain that, unless special precautions are taken, the diphenylcyanoarsine formed will, on keeping, undergo change owing to catalytic hydrolysis.

It is desirable that the hydrolysis of diphenylcyanoarsine should be examined more fully than has been described in the present paper, in order that conditions may be arrived at whereby the substance does not undergo alteration on keeping.

Action of Chlorine on Diphenylcyanoarsine.

The action represented by the equation

$$Ph_2As{\cdot}CN + Cl_2 = Ph_2As(CN)Cl_2,$$

was investigated.

Twenty grams of diphenylcyanoarsine were dissolved in 100 c.c. of benzene, and a current of chlorine was passed through the cooled solution. Solid began to separate, and the passage of the chlorine was continued until the liquid was green in tint. On removal, the solid fumed in air; it melted indefinitely at about 115°, and contained chlorine but no nitrogen. On boiling with water, it dissolved, and, on cooling, needles of diphenylarsinic acid separated. It seems likely that the compound in question was diphenylarsenic oxychloride, $(Ph_2AsCl_3)_2O$, which melts at 117° (La Coste and Michaelis, *Annalen*, 1880, **201**, 230), produced by the hydrolysis of the cyano-group, thus:

$$Ph_2AsCl_2{\cdot}CN + H_2O = Ph_2AsCl_2{\cdot}OH + HCN,$$
$$2Ph_2AsCl_2{\cdot}OH = H_2O + Ph_2AsCl_2{\cdot}O{\cdot}Ph_2AsCl_2,$$

whilst its conversion into diphenylarsinic acid would be interpreted as follows:

$$Ph_2AsCl_2{\cdot}O{\cdot}Ph_2AsCl_2 + 4H_2O = 4HCl + Ph_2As(OH)_2{\cdot}O{\cdot}Ph_2As(OH)_2,$$
$$Ph_2As(OH)_2{\cdot}O{\cdot}Ph_2As(OH)_2 + 2HCl = H_2O + 2Ph_2AsCl(OH)_2,$$
$$Ph_2AsCl(OH)_2 + H_2O = HCl + Ph_2As(OH)_3,$$
$$Ph_2As(OH)_3 = H_2O + Ph_2AsO{\cdot}OH.$$

When the addition of chlorine to diphenylcyanoarsine was con-

ducted with dry benzene or dry carbon tetrachloride as the solvent, a similar result was obtained.

On allowing the benzene filtrate in the first experiment to remain for several days at the ordinary temperature, a crystalline product was gradually deposited, which softened at 123° and melted at 127°. It amounted to 2 grams, and contained both nitrogen and chlorine. Another quantity of this substance was obtained from a similar experiment, the difference between it and the first sample being in the somewhat higher melting point, namely, 130—133°. The product, in fact, appeared to be *diphenylcyanoarsine dichloride*, $Ph_2As(CN)Cl_2$.

Found: Cl = 22·0.

$C_{13}H_{10}NCl_2As$ requires Cl = 21·8 per cent.

When once it had been isolated, it was apparently fairly stable when dry, since it underwent no change when kept in a desiccator for three weeks. When boiled with water, it dissolved completely, and needles of diphenylarsinic acid separated on cooling, as represented by the equations

$$Ph_2As(CN)Cl_2 + 3H_2O = HCN + 2HCl + Ph_2As(OH)_3,$$
$$Ph_2As(OH)_3 = H_2O + Ph_2AsO{\cdot}OH.$$

Action of Sodium Hydrosulphide on Diphenylchloroarsine.

This action was studied in order to ascertain if diphenylarsine hydrosulphide could be formed, thus:

$$Ph_2AsCl + NaSH = Ph_2As{\cdot}SH + NaCl.$$

The product consisted, however, of diphenylarsenious sulphide, which was presumably formed by the elimination of hydrogen sulphide from the hydrosulphide:

$$2Ph_2As{\cdot}SH = H_2S + Ph_2As{\cdot}S{\cdot}AsPh_2.$$

The yield was 83 per cent. of the theoretical.

The authors desire to acknowledge the valuable assistance rendered by Miss Agnes Paterson Millar, B.Sc. (Mrs. Cleland), Miss Nellie Walker, M.A., B.Sc., and the late Mr. George Fyfe Elder.

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, March 11th*, 1920.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 25TH, 1920, AT 5 P.M.

Sir JAMES J. DOBBIE, M.A., D.Sc., F.R.S., President, in the Chair.

Dr. H. BASSETT and Mr. A. STEVENSON were elected Scrutators, and the ballot for the election of Officers and Council was opened.

The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending December 31st, 1919, was proposed by Dr. F. L. PYMAN, seconded by Mr. E. GRANT HOOPER, and carried.

REPORT OF COUNCIL, 1919—1920.

A substantial addition to the number of Fellows was reported for 1918, and the Council is gratified to record a still greater increase during the past year. On December 31st, 1918, the number of Fellows was 3,401. During 1919, 274 were elected and 18 reinstated, making a gross total of 3,693. The Society has lost 43 Fellows by death, 42 resignations have been received, the election of 1 has been declared void, and the names of 38 have been removed for non-payment of Annual Subscription. The total number of Fellows, therefore, on December 31st, 1919, was 3,569, showing a net increase of 168, as against 131 the previous year.

It is with deep regret the Council has to report that the following Fellows have died:

Herbert Anderson (1895).
William Beam (1903).
David Bendix (1874).
Richard Blenkinsop (1902).
Arthur Anderson Bones (1912).
John Richard Brooke (1900).
Adrian John Brown (1876).
Herbert Stoddard Coleman (1913).
William James Cousins (1885).
Sir William Crookes (1857).
Walter Henry Dixon (1912).
William Lofland Dudley (1890).
Owen Charles Edwards (1918).
Arthur Henry Elliott (1878).
Philip Anderson Estcourt (1888).
Thomas Fairley (1865).

George Carey Foster (1856).
William Humphrey Gibson (1888).
Harold Cecil Greenwood (1916).
Samuel Godfrey Hall (1899).
Augustus George Vernon Harcourt (1859).
John Holmes (1897).
Henry Owen Huskisson (1861).
George Frederic Kendall (1884).
John Falconer King (1876).
Edward Gurley Love (1882).
Thomas Morison Maben (1915).
James Baird MacLachlan (1916).
George Martineau (1871).
Arthur Sampson Napier (1874).
William Henry Oates (1893).
Walter Parker (1917).
Francis Reginald Power (1884).
Sir Boverton Redwood (1866).
Norman Scott Rudolf (1909).
Alfred Ulrich Max Schlaepfer (1918).
John Emilius Lancelot Shadwell (1880).
Harry Shulman (1915).
Sir Peter Wyatt Squire (1882).
James Fleming Stark (1870).
John Charles Umney (1893).
Elwyn Waller (1878).
Christopher Joseph Whittaker (1899).

The Council has to mourn the loss of three Past-Presidents, Sir William Crookes, O.M., Dr. A. G. Vernon Harcourt, and Prof. J. Emerson Reynolds. Obituary notices of these and other Fellows will appear in the Transactions in due course.

Resignations have been received from:

Paul Seidelin Arup (1906).
Thomas James Bandinel (1916).
Frank Bayley (1917).
William Charles Trevor Beasley (1917).
John Cardew Bedwell (1901).
William Berry (1888).
Wilfred William O. Beveridge (1903).
Robert Bickerstaffe (1908).
William George Brown (1884).
Alexander Caruth (1913).
Pinzen Cheng (1915).
Joseph Morgan Davey (1905).
John Arthur Dewhirst (1899).
Edward Percy Frankland (1912).
George Pomeroy Furneaux (1909).
Henry Wippell Gadd (1901).
George Harrison Gemmell (1885).
Stanton Gibson (1913).
Arthur Frank Girvan (1908).
Alfred Rowland Gower (1893).
Herbert Green (1878).
Edgar Percy Hedley (1906).
Arthur Edward Holme (1895).
Robert John Hughes (1918).
Edgar Jobling (1912).
James Johnstone (1896).
Charles John J. Mansford (1897).
Frank Clifford Marchant (1913).
Robert Mills (1911).
John Charles Henderson Mingaye (1887).
Louis Murgatroyd (1907).
Frank Henry Pugh (1917).
Louis John Ezekiel Riley (1904).
Conrad Howard Rogers (1916).
John George Rose (1910).
William Charles Ross (1902).
Ernest William Smith (1910).
James Thomas Stevenson (1909).
Alan West Stewart (1914).
Cedric Gerard Verver (1917).
Alexander Watt (1877).
William Henry Withey (1908).

The congratulations of the Society are offered to Mr. Thomas Fogg, who, having been elected on November 17th, 1859, has completed sixty years as a Fellow, and to the following, who have attained their jubilee as Fellows:

	Elected.
William Henry Deering	April 1st, 1869.
James Thomson Bottomley	April 15th, 1869.
William James Lewis	Nov. 4th, 1869.
George Robertson Hislop	Jan. 20th, 1870.
David Brown	Mar. 17th, 1870.
Alexander Muirhead	Mar. 17th, 1870.

Since the last Annual General Meeting, the Society has lost two Honorary and Foreign Members, Prof. A. P. N. Franchimont and Prof. Alfred Werner. Sir Edward Thorpe and Prof. G. T. Morgan, respectively, have undertaken to prepare obituary notices of these distinguished chemists.

The volume of Transactions for 1919 contains 1,517 pages, of which 1,392 pages are occupied by 139 memoirs, the remaining 125 pages being devoted to Obituary Notices, lectures on special subjects, the Report of the Annual General Meeting, the Presidential Address, and the Report of the International Committee on Atomic Weights. The volume for the preceding year contained 89 memoirs, occupying 849 pages. The Journal for 1919 contains also 2,534 abstracts, occupying 1,148 pages, whilst the abstracts for 1918 numbered 2,436 and occupied 1,032 pages. In the last Report, in referring to the great and continuous decrease since the start of the war in the number of memoirs published in journals devoted to chemistry and allied subjects, the view was expressed that the lowest point had probably been reached and that an increase in the number of papers abstracted might be anticipated. This view has been justified; the number has shown a decided increase, especially in the latter part of the year, and a very considerable increase seems to be indicated for 1920.

The abstracts may be classified as follows:

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	—	823
Physiological Chemistry	—	144
Chemistry of Vegetable Physiology and Agriculture	—	186
	616	1,153
PART II.		
General and Physical Chemistry	—	636
Inorganic Chemistry	—	239
Mineralogical Chemistry	—	57
Analytical Chemistry	—	449
	532	1,381
Total in Parts I. and II.	1,148	2,534

In connexion with the revision of the Bye-laws, to which refer- ince was made in the last Report of Council, an Extraordinary ;eneral Meeting of the Society was held on May 8th, 1919. At his meeting, eight resolutions dealing with various modifications f the constitution of the Society were passed (see Proc., 1919,). 59), and the Council was authorised to secure a supplemental Charter giving the power to make the necessary alterations in the Bye-laws. The petition praying for such supplemental Charter was presented to the Privy Council last July, and His Majesty has now been graciously pleased to grant the request of the Society. The supplemental Charter has been received, and an Extraordinary General Meeting will be summoned at an early date to consider the alterations in the Bye-laws proposed by the Council under the new conditions.

Reference was made in last year's Report to the question of he publication of Chemical Compendia in the English language. The scheme set forth in the Report of the General Committee of he Chemical and Allied Societies was at a later date duly approved by the Council, and its further development was placed in the hands of the Federal Council for Pure and Applied Chemistry. The decision of the Council was communicated to the French and American Chemical Societies, to those societies represented on the General Committee, and to the Department of Scientific and Indus- ial Research, which later intimated that it would be prepared consider an application from the Federal Council for financial ssistance.

The question of the supply of chemical glassware and fine hemicals for research purposes, raised by the Department of cientific and Industrial Research, has received the earnest atten- ion of the Council. Its considered opinion on these matters as communicated to the Department of Scientific and Industrial esearch, and the views of the Council were expressed in greater etail by a deputation which waited on the Department.

The Council have accepted from the Harrison Memorial Com- ttee the administration of a Trust Fund for Research purposes l of a Memorial to the late Lieut.-Colonel E. F. Harrison, M.G., Director of the Chemical Warfare Department of the nistry of Munitions. A position for the memorial has been ind on the upper part of the arch outside the Meeting Room, d it is intended that the names of all those Fellows who fell action or died on service shall appear in close proximity to e memorial.

A collection of letters and portraits received by the late Sir Henry Roscoe from eminent scientific men of his time has been pre-

sented to the Society by Miss Roscoe, to whom the Council has expressed its appreciative thanks for this interesting and valuable gift.

The first of the three Lectures arranged by the Council to be delivered during the present Session was given on December 18th by Prof. James Walker, who chose as his subject "War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes." The lecture on "Some War-time Efforts in Chemical Industry at Gretna," which was to have been delivered on March 4th by Mr. John C. Burnham, has been unavoidably postponed. The third of the series will be given on June 17th by Prof. J. C. McLennan, who will lecture on "Helium." The Council is gratified to find that the delivery of lectures on special subjects continues to meet with appreciation from the Fellows, and regrets that the seating accommodation afforded by the Meeting Room is inadequate for these occasions.

Prof. A. W. Crossley and Dr. A. Scott have consented to act as the Society's representatives on the Conjoint Board of Scientific Societies, whilst Prof. H. E. Armstrong, Sir William J. Pope, and Sir William A. Tilden have been reappointed as the Society's representatives for the current year on the Federal Council for Pure and Applied Chemistry. The Council has further nominated Dr. J. C. Cain, Mr. A. J. Greenaway, Mr. C. A. Hill, Prof. J. M. Thomson, and Prof. F. Soddy to serve on the Sub-Committees of the Imperial Mineral Resources Bureau.

The Celebrations held by the French Chemical Society in Paris on June 5th and 6th, 1919, were attended by Sir William J. Pope as the Society's representative.

Permission was given to Dr. Kling, Director of the Laboratoire Municipale de Paris, to issue a French translation of the Annual Reports for 1918, and this was published in the early part of 1920 by Messrs. Gauthier-Villars et Cie.

At the request of the American Chemical Society, the Council has appointed a Committee, consisting of the Officers and the Editors, to co-operate with corresponding Committees appointed by the American Chemical Society and the Society of Chemical Industry to consider questions of Nomenclature, Spelling, and Pronunciation.

At the suggestion of Prof. P. A. Guye, the Council has agreed to refer the question of publishing Tables of Physico-Chemical Symbols to the Union Internationale de la Chimie Pure et Appliquée.

The Council desires to record its thanks to those Fellows who have contributed to Vol. XVI. of the Annual Reports, and to the Abstractors for their services during the past year.

A circular was issued to Fellows on January 23rd, 1920, stating that, subject to sufficient support being received, it was proposed to hold a Soirée at the Natural History Museum on the evening of Thursday, March 25th, the day of the Annual General Meeting. Owing, however, to insufficient support being forthcoming, the Council was reluctantly compelled to abandon the proposal.

The scheme for the extended use of the Library has now been in full operation since May 1st, 1919, and the fact that during the additional hours of opening the Library, 1,198 attendances were recorded, affords evidence that these extra facilities are appreciated. As already announced, the Library is now open until 9 p.m. every week-day except Saturday, when it closes at 5 o'clock.

The expenditure incurred during 1919 in enlarging the scope of the Library amounted to £439, of which sum £406 10*s*. was received from the following Societies: Association of British Chemical Manufacturers, Biochemical Society, Faraday Society, Institute of Chemistry, Society of Chemical Industry, Society of Dyers and Colourists, and the Society of Public Analysts. It is estimated that from £550 to £600 will be required to continue the scheme during 1920.

The number of books borrowed from the Library during 1919 was 2,867, as against 2,905 in 1918. The additions to the Library comprise 189 books, 338 volumes of periodicals, and 86 pamphlets, as compared with 126, 255, and 31, respectively, the previous year.

The accounts for the year 1919 show a balance of income over expenditure amounting to £522 3*s*. 3*d*., as against £2,489 4*s*. 4*d*. reported last March for the previous year, and it is now necessary to recognise that the prevailing high costs are rapidly overtaking the economies due to diminished printing during the War. Thus, although the income from all sources amounts to £11,838 1*s*. 7*d*., and exceeds that recorded for 1918 by £1,755 6*s*. 8*d*., the expenditure has increased by £3,722 7*s*. 9*d*., reaching the sum of £11,315 18*s*. 4*d*.

On examining the details of income and expenditure, it will be found that the increase of revenue arises from additional life compositions £263, admission fees £148, and subscriptions £315, together with £138 15*s*. 5*d*. from interest on increased investments, £417 12*s*. 4*d*. from sale of publications, and £574 14*s*. 11*d*. representing increased gross proceeds from advertisements in the JOURNAL.

The very serious increase of £3,722 7*s*. 9*d*. in expenditure is owing principally to the cost of the Society's publications, which aggregates £8,034 13*s*. 5*d*., as against £5,247 11*s*. 9*d*. for 1918, an excess of £2,787 1*s*. 8*d*. This is in some measure due to the

expected partial recovery in the volume of Transactions, as indicated by the following synopsis:

	Number of Pages.		
	Trans.	Abstr.	Total.
1914	2,909	2,068	4,977
1915	1,862	1,944	3,806
1916	1,368	1,532	2,900
1917	1,128	1,308	2,436
1918	995	1,032	2,027
1919	1,517	1,148	2 665

In so far as this represents an increased production of original work, it is a gratifying feature of the Peace year, but the enhanced cost of printing the JOURNAL, which rose from £2,750 8*s*. 3*d*. in 1918 to £4,625 2*s*. 7*d*. in the year under review, is the cause of grave anxiety to the Council. At its request, the situation has been explored by the Finance Committee, but it has not been found possible to devise any practicable remedy; it appears from the inquiry that the position of the Society is less unfavourable than that of some other similar bodies. Nevertheless, the fact that the cost of the JOURNAL per page has now reached £2 4*s*. 8*d*., in comparison with 17*s*. 9*d*. in 1914, will shortly become the source of deep embarrassment, because a return to pre-war volume unaccompanied by a diminution in cost of production would confront the Society with an expenditure of £12,000 on the JOURNAL alone, involving a deficit approximating to £4,000 per annum.

Having regard to this forecast, the Council considers it a duty to urge upon authors the most rigid observance of word-economy in expressing their ideas and the restriction of experimental details within the smallest possible compass.

The necessity of increasing the remuneration made to the staff has been the principal cause of a rise in administrative expenses from £1,681 6*s*. 5*d*. in 1918 to £2,220 7*s*. 4*d*. in 1919.

£2,000 National War Bonds were purchased early in the year, and £480 invested in Funding Loan, but the estimated value of the Society's investments on December 31st, 1919, was only £1,291 10*s*. 10*d*. higher than at the corresponding date a year before.

The following grants have been made from the Research Fund during the year:

The physical chemical properties of beryllium compounds.
A. J. Allmand.. £10 0 0

The formation of binary and ternary mixtures of constant minimum boiling point in a group of organic liquids.
W. R. G. Atkins.. 10 0 0

Formation and stability of spiro-compounds. O. Becker ...	£15	0	0
(*a*) Physiologically active bases. (*b*) Spirane bases with a view to resolution into optically active components. G. M. Bennett	5	0	0
Oximino-derivatives. O. L. Brady................................	10	0	0
The biochemistry of iodine. A. T. Cameron....................	15	0	0
Action of sulphuretted hydrogen on organic compounds containing unsaturated linkages. F. Challenger	10	0	0
The constitution of carbazole blue. M. Copisarow	20	0	0
Study of the addition of alkyl haloids to ethyl β-diethylaminocrotonate. P. W. Denny	10	0	0
Derivatives of xanthene. S. N. Dhar	10	0	0
Isomerism of the oximes. F. P. Dunn	10	0	0
Ring formation of organic compounds. E. H. Farmer	15	0	0
The constitution of weak acids and their salts. J. C. Ghosh	30	0	0
(*a*) Preparation of substituted glutaric acids. (*b*) Constitution of Guareschi's spiro-compounds. W. H. Gough	15	0	0
Action of halogens upon dichlorodimethyl*cyclo*hexadiene. L. E. Hinkel...	15	0	0
Condensation of ethyl sodiomalonate with glycolchlorhydrin. J. Kenner...	10	0	0
The solubility relationships of 4-dimethylamino-1-phenyl-3-methylpyrazole. H. King..................................	5	0	0
Formation of ketones from acids of the glutaric series and the formation of bridged-ring compounds. G. A. R. Kon...	15	0	0
The properties of certain binary mixtures of liquids. J. I. O. Masson	10	0	0
A quantitative method of determining the velocity of coagulation. J. N. Mukherjee	15	0	0
The reactivity of sulphur chloride with amino- and amido-compounds. K. G. Naik	10	0	0
Attempted synthesis of myricetin. M. Nierenstein	10	0	0
Action of diazomethane on α-diketones and on acyl chlorides. M. Nierenstein..	15	0	0
The investigation of gallotannin (contd.). M. Nierenstein...	15	0	0
The relationship between melting point, chemical composition and physical properties of series of organic compounds. P. W. Robertson	8	0	0
The latent heat of fusion of palmitic acid and other fatty acids. (Mrs.) K. Stratton......................................	20	0	0
The conversion of borneol into camphene and the study of analogous reactions. (Miss) M. Tadman	10	0	0
Influence of the constitution of tertiary bases on the rate of formation of quaternary ammonium salts (contd.). E. R. Thomas	15	0	0
Total	£358	0	0

Whilst the aggregate grants exceeded by £261 14*s*. 0*d*. the corresponding payments for 1918, the balance of income over expenditure for 1919 is £349 13*s*. 11*d*., as against £539 13*s*. 9*d*. for the

previous year. The return on investments was £24 6*s*. 5*d*. higher, and £91 0*s*. 10*d*. was realised by sale of gold and platinum; on the other hand, the repayment of grants was £44 14*s*. 6*d*. less than during 1918, and the recovery of income-tax was £13 5*s*. 4*d*. lower. £300 National War Bonds were purchased for this account in 1919.

A vote of thanks to the Auditors, proposed by the TREASURER and seconded by Mr. F. G. POPE, was carried unanimously, Dr. C. K. TINKLER making acknowledgment.

Professor H. BRERETON BAKER proposed a vote of thanks to the Treasurer, Secretaries, and Council for their services during the past year. This was seconded by Dr. T. SLATER PRICE, and acknowledged by Professor S. SMILES, the retiring Secretary.

The PRESIDENT then delivered his Address, entitled, "The War and Key Industries, with special reference to the Fixed Nitrogen Industry."

A vote of thanks to the President for his services in the Chair during the past year and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions, was proposed by Sir WILLIAM A. TILDEN, and seconded by Dr. ALEXANDER SCOTT. The motion was carried with acclamation, and acknowledged by the PRESIDENT.

The Scrutators presented their report, and the PRESIDENT declared the following to have been elected as Officers and Council for the ensuing year:

President. Sir James Johnston Dobbie, M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, C.B.E., M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Julius Berend Cohen, Ph.D., B.Sc., F.R.S.; Frederick George Donnan, M.A., Ph.D., F.R.S.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Samuel Smiles, O.B.E., D.Sc., F.R.S.; James Walker, D.Sc., LL.D., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Liabilities.

	£ s. d.	£ s. d.
To Subscriptions received in advance	424 0 0	
,, ,, ,, ,, (Lady Subscriber)	1 10 0	
		425 10 0
,, Sundry Creditors		1914 1 5
,, Current Account Overdrawn		250 4 1
,, Research Fund:—		
As per last Balance Sheet	14896 17 1	
Add Excess of Income over Expenditure for the year	349 13 11	
		15246 11 0
,, Chemical Society: Excess of Assets over Liabilities:—		
As per last Balance Sheet...	27247 11 9	
Add Excess of Income over Expenditure for the year	522 3 3	
		27769 15 0
		£45606 1 6

Assets.

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£6730 Metropolitan Consolidated $3\frac{1}{2}$ per cent. Stock	7212 8 6	
£1050 London and North Western Railway 3 per cent. Debenture Stock	839 12 0	
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India $2\frac{1}{2}$ per cent. Stock	1316 1 0	
£2400 Bristol Corporation $2\frac{1}{2}$ per cent. Debenture Stock	2070 2 0	
£4341 Midland Railway $2\frac{1}{2}$ per cent. Preference Stock	3572 2 5	
£1200 Leeds Corporation 3 per cent. Debenture Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460 13 6	
£1200 North British Railway 3 per cent. Debenture Stock	1088 11 0	
£700 Canada $3\frac{1}{2}$ per cent. Stock, 1930/50	704 8 6	
£2100 5 per cent. War Stock, 1929/47 } £5100 5 per cent. War Bonds }	7040 0 2	
£600 4 per cent. Funding Loan, 1960/90	480 0 0	
(Estimated present value of Investments, £20,538 5*s.* 3*d.*)		28522 0 1
,, Sundry Debtors		1506 8 0
,, Subscriptions in Arrear estimated to realise		270 0 0
,, Insurance paid in advance		47 10 10
,, Cash in hand		14 11 7
,, Research Fund:—		
Investments (value when acquired):		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010 0 0	
£4400 Metropolitan Consolidated $3\frac{1}{2}$ per cent. Stock	4587 18 0	
£1034 Great Western Railway $2\frac{1}{2}$ per cent. Debenture Stock	1049 15 11	
£1142 16*s.* New South Wales 3 per cent. Stock ...	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
£1365 Midland Railway $2\frac{1}{2}$ per cent. Debenture Stock	1010 0 9	
£806 Victoria 3 per cent. Stock	706 6 2	
£4498 11*s.* 0*d.* 5 per cent. War Stock	4267 4 10	
£300 5 per cent. War Bonds, 1928...	300 0 0	
		14934 2 5
(Estimated present value of Research Fund Investments, £11,549 8*s.* 1*d.*)		
,, Cash at Bank...		312 8 7
		£45606 1 6

Q*

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, QUEEN VICTORIA STREET, E.C.
March 1st, 1920

Approved—ARTHUR R. LING,
GEORGE SENTER,
C. K. TINKLER.

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions				612	0	0
,, Admission Fees				1101	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1919	232	0	0			
,, during 1919 ,, ,, ...	5211	0	0			
,, ,, ,, ,, 1918	378	0	0			
,, ,, ,, ,, 1917 and previous	64	0	0			
	5885	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	460	0	0			
	5425	0	0			
Add Arrears at date: 1919, £388; 1918 and previous, £390, estimated to realise as per Balance Sheet	270	0	0			
				5695	0	0
,, Lady Subscribers				12	0	0
,, Investments:—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...	182	11	3			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock	22	1	0			
,, £1520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock ...	31	18	8			
,, £1400 India 2½ per cent. Stock	27	2	6			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	42	0	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock	76	12	11			
,, £1200 Leeds Corporation 3 per cent. Debenture Stock ...	25	4	0			
,, £1500 Transvaal 3 per cent Guaranteed Stock, 1923/53	38	5	0			
,, £1200 North British Railway 3 per cent. Debenture Stock	25	4	0			
,, £700 Canada 3½ per cent. Stock 1930/50	19	12	0			
,, £7200 5 per cent War Stock and War Bonds...	307	1	2			
,, £600 4 per cen Funding Loan, 1960-90	5	15	11			
Income Tax Recovered	189	10	6			
,, Interest on Deposit Account	26	4	6			
				1019	3	5
Publication Sales:—						
Journals	2048	14	3			
Proceedings	20	19	2			
Collective Index	80	4	8			
Library Catalogue	1	16	11			
Atomic Weight Tables	1	13	9			
Annual Reports on Progress of Chemistry	320	5	0			
Memorial Lectures	5	18	3			
Jubilee Volumes	0	5	0			
	2479	17	0			
Less Publishers' Commission	241	9	7			
				2238	7	5
,, Proceeds of Advertisements in Journal	1015	1	6			
Less Commission	66	6	11			
				48	14	7
,, Miscellaneous Receipts				26	1	2
,, Subscriptions from other Societies				42	0	0
,, Donations to Library				40	15	0
				£11,838	1	7

FOR THE YEAR ENDED 31ST DECEMBER, 1919.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal :—		
Salary of Editor, including Indexing ...	620 0 0	
Salary of Sub-Editor and Assistant ...	250 0 0	
Editorial Postages ...	23 0 9	
Abstractors' Fees ...	393 9 10	
Printing of Journal ...	4625 2 7	
Banding ...	147 18 0	
Printing of Advertisements ...	296 14 9	
Wrappers and Addressing ...	8 3 10	
Distribution of Journal ...	678 16 6	
Authors' Copies ...	186 15 5	
Insurance of Stock ...	16 4 0	
		7246 5 8
,, Anniversary Dinner ...		32 16 4
,, Annual Reports on the Progress of Chemistry ...		542 15 1
,, Purchase of back numbers of Journal ...		15 14 6
,, List of Fellows ...		245 12 7
,, Library Expenses :—		
Salaries ...	639 15 6	
Books and Periodicals ...	259 14 2	
Binding ...	50 6 6	
		949 16 2
,, Indexing for International Catalogue ...		30 0 0
,, Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological ...	10 0 0	
,, Donation to Board of Scientific Societies...	5 5 0	
,, Federal Council for Pure and Applied Chemistry ...	12 0 0	
,, Middlesex Hospital ...	5 5 0	
		32 10 0
,, Administrative Expenses :—		
Salary of Staff ...	685 11 6	
War Bonus ...	435 6 11	
Wages (Commissionaire, Housekeeper, and Charwoman) ...	283 12 3	
Coal and Lighting ...	88 10 5	
House Expenses and Repairs ...	105 18 8	
Tea Expenses ...	50 5 10	
Insurances ...	17 2 0	
Accountants' Charges ...	21 0 0	
Commission on Recovery of Income Tax ...	9 9 6	
Miscellaneous Printing ...	191 0 1	
Stationery ...	157 9 10	
Postages...	122 4 1	
Advertisements of Meetings ...	10 16 6	
Miscellaneous Expenses ...	41 19 9	
		2220 7 4
Balance, being excess of Income over Expenditure carried to Balance Sheet ...		522 3 3
		£11,838 1 7

Research Fund Income and Expenditure Account for the Year ended 31st December, 1919.

Income.

	£ s. d.	£ s. d.
To Dividends on:—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock ...	28 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	119 7 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	18 1 10	
£1142 16s. New South Wales 3 per cent. Stock...	29 2 10	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	23 11 4	
£1365 Midland Railway 2½ per cent. Debenture Stock ...	23 17 8	
£606 Victoria 3 per cent. Stock ...	16 18 6	
£4498 11s. 0d. 5 per cent. War Loan, 1929-47 ...	224 18 6	
£300 5 per cent. National War Bonds, 1928 ...	9 16 0	
		493 13 8
,, Proceeds of Sale of Platinum and Gold ...		91 0 10
,, Repayment of Grants ...		36 15 7
,, Income Tax Recovered ...		93 14 7
		£715 4 8

Expenditure.

	£ s. d.
By Grants ...	358 0 0
,, Commission on Recovery of Income Tax ...	4 13 9
,, Advertisements ...	2 17 0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet ...	349 13 11
	£715 4 8

Secretaries.—James Charles Philip, O.B.E., M.A., D.Sc., Ph.D.; Henry Rondel Le Sueur, D.Sc.

Foreign Secretary.—Arthur William Crossley, C.M.G., C.B.E., D.Sc., F.R.S.

Ordinary Members of Council.—Arthur John Allmand, M.C., D.Sc.; Edward Frankland Armstrong, D.Sc., Ph.D.; Julian Levett Baker; Francis Howard Carr; Alexander Findlay, M.A., D.Sc., Ph.D.; Francis Ernest Francis, D.Sc., Ph.D.; John Addyman Gardner, M.A.; John Millar Thomson, LL.D., F.R.S.; James Colquhoun Irvine, D.Sc., Ph.D., F.R.S.; Charles Alexander Keane, D.Sc., Ph.D.; Sir Robert Robertson, K.B.E., M.A., D.Sc., F.R.S.; Edward William Voelcker.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 25th, 1920.

By SIR JAMES J. DOBBIE, M.A., D.Sc., LL.D., F.R.S.

The War and Key Industries, with special reference to the Fixed Nitrogen Industry.

IT is my privilege to address you for the first time as President in the year in which the war has been declared officially at an end. Whether the peace which we have achieved is to usher in a new era of greatness and prosperity for our country or to mark the beginning of its decline will depend on the thoroughness with which we have learned the lessons of the great war and with which we are prepared to apply them.

Amongst these lessons there is none more important than that which concerns the dependence on foreign countries of home industries that are vital to the safety of the State. The war has taught us that a sound national policy requires us in future to produce or have the means of producing within our own country many articles which formerly we obtained exclusively from abroad. From a general survey of our industries it will be seen that they form a highly complex system in which certain products are essential to the manufacture of others. When these essential products cease to be available the industries dependent on them are necessarily brought to a standstill. Industries which are in this way essential to others are now commonly known as "key" industries, one of the many terms to which the war has given birth or at any rate to which it has given wide currency for the first time. When such industries are carried on exclusively abroad it is obvious that the existence of the industries in this country which depend on them must be jeopardised in time of war, and we have had many illustrations of this danger in the course of the last five years. On the outbreak of war it was discovered that we were entirely dependent on enemy sources for certain kinds of optical glass used in the construction of instruments required for war service, and the manufacture of such instruments was in consequence seriously interfered with. Again, the failure of the usual

supplies of coal-tar dyes threatened a large section of our textile industries with ruin. So alarming was the position thus created that the Government speedily realised the necessity for intervention, and under its ægis and with its financial assistance the movement which now promises such rich results was inaugurated for the revival in this country of the manufacture of coal-tar dyes. The recognition by Government that it is the duty of the State, in such circumstances as I have described, to intervene, is perhaps one of the most significant and far-reaching consequences of the war so far as our industries are concerned. Many difficult and delicate economic questions will undoubtedly arise in the future in connexion with "key" industries, and it is important that claims for the special treatment of these should be put forward only where some truly national interest is at stake.

The publication of the Report of the Nitrogen Products Committee of the Munitions Inventions Department has recently directed attention prominently to the group of industries concerned with the synthetic production of ammonia, nitric acid, and other compounds of nitrogen. It is unnecessary for me to dwell on the importance of these compounds in their relation especially to agriculture and to the manufacture of munitions of war. Without them our agriculture would languish, and we should lack the means of producing those explosives which are most essential to the conduct of modern warfare. Yet before the end of the war our supply of ammonia was running short, and our stock of sodium nitrate could only be replenished with ever-increasing difficulty.

The Report of the Nitrogen Products Committee closes with the following observation:

"As far as the United Kingdom is concerned, nitrogen-fixation and allied processes will constitute a new 'key' industry."

This conclusion is one of enormous importance to our country, and I have thought it might be useful this afternoon to examine briefly the grounds on which it is based and endeavour to emphasise some of the lessons which may be learned from the Committee's Report.

Before the war there was no nitrogen question in this country. We were then producing about five times as much ammonium sulphate as we required for our own use, and our production was increasing at a greater rate than our consumption. In such circumstances there seemed to be no cause for anxiety with regard to the future.

The main facts relating to the supply and disposal of the various forms of fixed nitrogen are simple, and as they are essential to a proper understanding of the nitrogen problem it will be convenient

to state them at once. We depend for ammonia almost entirely on the by-products of the gas works and coke ovens, and for sodium nitrate on our imports from Chile. Taking the average of the years 1911–13 our annual production of ammonium sulphate (25 per cent. NH_3) was 393,927 tons, of which we retained only 70,454 tons for our own use, exporting 323,473. Our average annual imports of sodium nitrate for the same period amounted to 130,997 tons.

In discussions relating to our nitrogen resources we are concerned not so much with the amounts of the various compounds containing nitrogen as with the total amount of the element. It is convenient, therefore, to express all quantities whether of ammonium sulphate, sodium nitrate, or cyanamide, in terms of nitrogen, and this plan has been followed with great advantage throughout the Committee's Report. In one of the tables entitled "Nitrogen Balance Sheet for the United Kingdom" the amount of combined nitrogen produced in this country or imported into it is shown on one side of the account, and the amount used in its industries or exported, on the other. It appears from this statement that for the period 1911–13 we produced annually on the average 82,404 tons and imported 23,979 tons of combined nitrogen, and that we exported 71,490 tons, retaining in the country for our own needs 34,893 tons. Although we are not concerned for the present with the disposal of the balance remaining in this country, it may be interesting to notice in passing what became of it. Agriculture absorbed by far the larger part—25,015 tons; the manufacture of sulphuric acid and explosives for mining and quarrying, 2885 and 1901 tons respectively; the manufacture of nitric acid, potassium nitrate, munitions of war, and fireworks together 2059 tons; the ammonia-soda and cold-producing industries, 1150 tons, leaving 1883 tons unaccounted for.

At first sight the position of Germany at the beginning of the war in regard to combined nitrogen does not seem to have differed much from our own. She obtained ammonia almost entirely from her gas works and coke ovens, but required nearly all she produced for her own purposes. Her margin for exportation in 1913 amounted to no more than 76,000 tons of sulphate. She drew her supplies of sodium nitrate, as we did, from Chile, but in consequence of the large extent of land under cultivation and her liberal use of nitrogenous fertilisers, her demand for nitrate was more than six times as great as ours, and in 1913 exceeded 800,000 tons.

When we look more closely we see that the positions, however similar superficially, differed profoundly. For some years prior to 1914 Germany had been manufacturing cyanamide on a limited scale, and not long before the outbreak of war the Haber process

for producing ammonia by the direct union of hydrogen and nitrogen had reached the stage at which its success as an industrial process was assured. She also possessed in the process which bears Ostwald's name the means of converting ammonia by oxidation into nitric acid. Thus there existed potentially in Germany the means of producing unlimited quantities of ammonia and nitric acid, whilst our supplies of ammonia were restricted by the output of our gas works and coke ovens, and we were entirely dependent for nitric acid on the importation of sodium nitrate. So far as these commodities, so necessary to her agriculture and to the conduct of the war, were concerned, Germany was self-contained and was in a position to supplement the ammonia which she obtained from by-product sources and to replace the sodium nitrate which she imported from overseas to any required extent by synthetic products. Although exact statistics are not obtainable, it is estimated that her production of calcium cyanamide, which was only 24,000 tons in 1913, had risen in 1917 to at least 400,000 tons, and within the same period her production of ammonium sulphate by the Haber process had increased from 30,000 tons to 500,000 tons. The development of the ammonia oxidation process in the course of the war was a still more remarkable achievement when it is remembered that it had only been tested on a comparatively small industrial scale when the war began. There is good reason to believe that by the middle of 1916 the amount of sodium nitrate produced by Ostwald's process was equivalent to more than a quarter of a million tons of nitric acid per annum.

The synthetic production of nitric acid was a necessity for Germany. By our blockade she was cut off from her overseas supplies of sodium nitrate, and had she been unable to make good the want from internal sources she would have been compelled to sue for peace as soon as her reserve stocks were exhausted. The development of the ammonia oxidation process alone made the war possible. It has been well said that this was a chemists' war.

As the war progressed it was not long before the weakness of our position became apparent. We have seen that at its commencement our production of ammonia was far in excess of our own requirements, and after our Navy had swept the German cruisers from the seas there seemed to be no longer any ground for anxiety as to the maintenance of our supplies of sodium nitrate. With the development of the submarine warfare, however, a new situation was created. The importation of nitrate was again endangered, and although we had still sufficient ammonia available to give us by oxidation all the nitrate we required, we possessed neither the plant nor the technical experience necessary to effect

the conversion. The sodium nitrate that continued to reach us was required to an ever-increasing extent for the manufacture of munitions, and soon there was none available for agriculture, and it was necessary to replace it for this purpose by ammonium sulphate. The substitution of ammonium sulphate for sodium nitrate as a fertiliser made a further heavy demand on our surplus stock of the sulphate. This was also being more and more depleted by the ever-growing requirements of the munition factories, especially after the introduction of amatol, which contains as much as 80 per cent. of ammonium nitrate, and it became necessary to restrict the exportation of ammonium sulphate. The amount exported, which reached 325,000 tons in 1913, fell in 1916 to 259,000 and in 1918 to 19,150 tons, but even this did not long suffice to allay anxiety with regard to the future. With the increasing destruction of our corn ships, the question of maintaining our food supplies became one of great urgency. Steps were taken to increase the area of cereal cultivation and at the same time to increase by heavier manuring the productivity of the land already under the plough. These measures made still further demands on our stock of ammonium sulphate, and it was recognised that the time was rapidly approaching when the ample margin existing at the beginning of the war would be exhausted and the country would be face to face with a shortage of ammonia. Before the war ended the shortage was actually making itself felt. According to a statement made to the Committee on behalf of the Board of Agriculture, 60,000 tons of ammonium sulphate more than was available could have been disposed of to farmers during the season June, 1917, to May, 1918.

Thus a situation had actually arisen which, had it been suggested at the beginning of the war, would have seemed too remote for serious consideration.

We know now that under the conditions of modern warfare we are exposed to a formidable danger against which we can only adequately protect ourselves by having at command the means of producing ammonia and nitric acid to any required amount within our own shores. This is the inevitable conclusion that is forced upon us by a study of the facts as they unfolded themselves in the course of the war.

Already in the early summer of 1916 the position was causing so much anxiety that with the sanction of the present Prime Minister, then Minister of Munitions, the Committee, afterwards known as the Nitrogen Products Committee, was appointed to report on the whole question of the fixation of atmospheric nitrogen with reference to the needs of the country and the Empire,

and on the steps necessary to conserve and increase the national resources in nitrogen-bearing compounds. Although by the terms of reference the scope of the Committee's inquiry extended to peace as well as to war conditions, the question that pressed for an immediate answer was how to increase our supply of ammonia, if necessary, during the war. Obviously one of the first steps was to examine into the possibilities connected with the existing sources of supply. The Committee, therefore, instituted an exhaustive inquiry into the conditions of the various industries in which ammonia is obtained as a by-product. Improvements in the existing practice of recovery from the gas works; the saving of the ammoniacal liquor which is at present allowed to run to waste from the smaller works; the replacement of the beehive ovens still extensively used in this country in coke-making by ovens adapted to the recovery of the ammonia produced in the process; the more extended use of coal gas and coke instead of raw coal for domestic and industrial purposes, were all considered, and suggestions under these various heads were made to the Ministry of Munitions. It was, however, clearly established that whilst a substantial increase of ammonia might ultimately be obtained from such sources, the immediate gain could not be great. As a matter of fact, the yield of by-product ammonia in this country increased by 26,000 tons between 1913 and 1917, the increase being due mainly to the substitution of recovery for beehive ovens.

Possible sources of supply not hitherto utilised, such as peat and sewage, were also reviewed, but no satisfactory method of obtaining ammonia from them on the industrial scale having yet been worked out, it was recognised that extensive investigation, probably extending over a long period, would have to be undertaken before the practicability of utilising them economically as sources of ammonia could be put to the proof.

It remained to inquire into the possibility, as a war measure, of installing one or other of the processes for the fixation of nitrogen which were in use on the Continent. Two things had to be considered in this connexion: the suitability of the various methods to the conditions of this country, and the time likely to be required for their installation, having regard, amongst other things, to the amount of preliminary experimental work involved. It was obvious that those processes which depend on the direct union of oxygen and nitrogen under the influence of the electric arc are unsuited to this country owing to the want of a cheap and abundant supply of water-power to produce the large amount of electric energy required. The production of calcium cyanamide, from which ammonia is readily obtained, also requires a large expendi-

ture of energy, although a relatively small amount per unit of nitrogen fixed, as compared with the arc processes. This, however, is counterbalanced to some extent by the abundance and cheapness of the limestone and anthracite required for its production.

Although cyanamide had never been manufactured in this country, the working details of the process were easily procurable, and the Committee felt justified, therefore, in recommending it for adoption as the one best suited to meet any shortage of ammonia that might occur during the war. This recommendation was at first adopted, but for reasons which I need not enter into now was not acted on.

From the date of the appointment of the Committee a staff of chemists and physicists, under the direction of Dr. J. A. Harker, was actively engaged in an experimental investigation of the conditions of the manufacture of ammonia by the Haber process, which had been introduced into Germany not long before the outbreak of war. This process requires the expenditure of only a comparatively small amount of power, and is therefore well adapted to the conditions of this country. It is simple in theory, consisting in the direct union of nitrogen with hydrogen in the presence of a catalyst at a high temperature and pressure. Those, however, who recall the lecture delivered by Haber at Liverpool in the early part of 1914 will appreciate the magnitude of the physical and mechanical difficulties that had to be overcome before the process attained technical success. Unfortunately, the working details were unknown to our chemists, and had to be studied experimentally both from the chemical and the engineering point of view. The selection of a suitable catalyst, the conditions under which it acts most efficiently, the effect of impurities, the conditions of temperature and pressure, the influence of the rate at which the gas passes through the apparatus upon the yield of ammonia, the best method of removing the ammonia produced, the physical problems connected with the circulation of gases at high pressures and velocities, were all subjected to systematic investigation. Moreover, the difficult problem of making provision for an abundant supply of cheap and pure hydrogen, which is indispensable to the process, had to be worked out at the same time. The new developments during recent years in the manufacture of hydrogen on a large scale for the hydrogenation of fats and oils, as well as for aviation purposes, give a special interest to the researches, carried out for the Committee, on catalytic processes for hydrogen production and purification.

These investigations were begun in the summer of 1916, and the results obtained by the beginning of the following year were con-

sidered so promising that the Committee included in an interim Report submitted to the Ministry of Munitions in February a recommendation for the erection of a trial plant. They were not, however, then prepared to put forward proposals for the establishment of the Haber process on an industrial scale. In October, 1917, however, the Explosives Department of the Ministry of Munitions felt justified by the results of the experimental work obtained by that date in recommending that this process should be adopted as the basis of a national factory for the production of fixed nitrogen, and the erection of a factory was actually in progress when the war ended.

Much successful experimental work had also been carried out on the oxidation process for the conversion of ammonia into nitric acid and ammonium nitrate, and it was proposed to include plant for these purposes in the national factory.

In the course of the experimental work carried out for the Committee many interesting and valuable observations were made and many important results, both from the scientific and technical point of view, were obtained. When the reports describing the investigations are published they will be found to constitute an addition of great value to the scientific and technical literature of the subject, and will form a lasting memorial to the skill and energy of the chemists and physicists who took part in them. Although no doubt something remained to be done on the engineering side, the fact that they should have succeeded in so short a time in bringing a process, which it cost the Germans so much time, trouble, and money to perfect, to the stage at which it was deemed fit for adoption by the Ministry of Munitions, was surely a notable achievement.

In this connexion I may perhaps be allowed to refer to the death of Dr. Harold Greenwood, a Fellow of this Society, who had charge from the beginning of the investigation of the synthetic ammonia problem, and whose exceptional ability and untiring energy contributed so largely to the important results obtained.

I have now traced the causes which led, as the war proceeded, to the gradual absorption of the surplus of ammonia which we produced in excess of our own needs in pre-war days, and I have described the action which was taken to meet the shortage which had actually begun to make itself felt in the course of the war.

If I have succeeded in making the position clear, you will realise that at the close of the war we were rapidly approaching a crisis as regards our supplies of combined nitrogen. Our huge surplus of ammonia had gone, and the demands of the munition factories and of agriculture were ever on the increase. On the

other hand, the importation of sodium nitrate was carried on under great difficulties, and the usual sources of our ammonia supplies were found to be incapable of any considerable expansion. In these circumstances surely the conclusion of the Committee is justified that nitrogen-fixation constitutes a "key" industry which is essential to our economic safety and to our national defence, and that it is one of those industries which should be established, if necessary, with the assistance of Government. In time of war complete independence of external supplies of combined nitrogen is a necessary condition of safety, and independence can only be secured if we have within the country the means of producing fixed nitrogen to any extent that may be required. Our potential sources of by-product ammonia are undoubtedly very large, but the practicability of making use of some of them has yet to be demonstrated, and the extent to which some of those which are known to be capable of utilisation can be made immediately available is very limited. On the other hand, although the processes for producing fixed nitrogen have not yet been established in this country, their installation could be quickly effected, and we should then be possessed of the means of indefinitely increasing our nitrogen production. To ensure the safety of the country, however, it is sufficient in the opinion of the Committee that we should possess experience of the working of the fixation processes and nucleus plant which would be capable of rapid extension.

Apart from the question of security in time of war, there are other reasons which render it in the highest degree important that the synthetic processes for the production of nitrogen compounds should be established in this country. The demand for combined nitrogen for purposes other than the manufacture of munitions of war is greater now than before the war, and is certain to expand still further. This is due to a variety of causes, but mainly to the increased requirements of agriculture. Our pre-war consumption of artificial nitrogenous manures of all forms was only equivalent to 25,000 tons of nitrogen. Towards the end of the war it had risen to 60,000 tons in consequence of the addition of nearly 4,000,000 acres to the land under the plough, and to the more intensive cultivation resorted to with the object of increasing the production of the soil. Unless we have already forgotten one of the lessons of the war we must continue to grow a larger proportion than formerly of the grain we require, and unless the money spent on agricultural education has been spent in vain we must expect an ever-increasing demand for artificial fertilisers. Assuming that the present acreage now under the plough is maintained and that nitrogenous manuring on a moderate scale is more gener-

ally resorted to, Dr. E. J. Russell estimates that eventually the equivalent of half a million tons of ammonium sulphate, or 100,000 tons of combined nitrogen, will be required annually for fertilising purposes alone. This increase might, no doubt, be met partly by increased importation of sodium nitrate, but, since our agriculture requires both forms of fertiliser, a large additional amount of ammonium sulphate must be obtained from some new source of supply or taken from what is at present available for exportation.

The maintenance of our export trade is of vital importance to the country, especially in present circumstances, but it is clear that we cannot both continue to export ammonium sulphate on the pre-war scale and meet the growing demands at home unless we increase our production of ammonia. In this connexion it is to be remembered that during the war Germany was manufacturing nitrogen products far in excess of her peace requirements, and that, with the plant now set free, she is probably in a position to compete with this country and with Chile in the nitrogen markets of the world. How far she will be able to do so successfully will depend on economic factors which are at present unknown. It is certain, however, that under pre-war conditions synthetic nitrogen compounds could be produced at prices which compared favourably with those at which ammonium sulphate and sodium nitrate were then sold. Should this still hold good, our export trade will be endangered unless we are in a position to oppose British to foreign synthetic products.

Having dwelt on the difficulties and dangers which during the ar threatened our industries dependent on nitrogen products, it satisfactory to be able to add that one of the most important commendations of the Committee is in a fair way of being ted on.

It is generally understood that the national factory at Billingam-on-Tees, the erection of which was begun in 1918, is about be acquired by an influential syndicate representing a large proortion of the heavy chemical trade of the country. It is the itention, I understand, to commence with a moderate-sized synetic plant in which many of the details will represent notable nprovements on existing German practice, and ultimately to evelop this into a very large commercial project. In addition, the anufacture of nitric acid and nitrates by the oxidation process ill form part of the scheme, and it will be possible to produce rom this source a considerable part of the national requirements f nitric acid for commercial purposes.

Such a combination of chemical interests opens up vast possibili-

ties for the more economic production of ammonia, by combining its manufacture with other industries in which the by-products of the Haber process could be utilised. The Solvay process, for example, in which large quantities of carbonic acid are required, is stated to be already in operation in Germany in association with the Haber process. Other developments may be looked for in connexion with the disposal of the large quantity of oxygen resulting from the production of nitrogen, and this, again, may lead to the recovery in quantity of the rarer elements of the air which are now coming into demand for technical purposes.

It is important, however, not only that effect should be given to the specific recommendations of the Committee with regard to the established processes, but also that the researches begun during the war on processes still in the experimental stage should be continued. Many branches of the problem still call for investigation both in the case of the by-product and the synthetic industries.

As an instance of the former I may mention the proposal to prepare a smokeless fuel for domestic use by carbonising coal at a low temperature under conditions which would allow of the recovery of the ammonia. This problem is now being investigated by the Fuel Research Board. Another interesting subject connected with the utilisation of by-products is the treatment of coal used at electric power stations for recovery of ammonia. Here the increased amount of fuel required when the by-products are recovered as compared with the amount required in direct firing must be set against the value of the by-products. You cannot have both the full heating value of the fuel and the by-products. This is a point too often overlooked when discussing the question of our potential supplies of ammonia.

Amongst the synthetic processes still in the experimental stage, which in the opinion of the Committee should be further investigated, is the interesting Häusser process, in which the heat of explosion of a mixture of combustible gas and air is utilised to bring about the union of nitrogen and oxygen without the large expenditure of electrical energy required by the arc processes. The exhaust gases from the explosion apparatus contain oxides of nitrogen which can be recovered by absorption in water. By this process both power and nitric acid can be obtained simultaneously. From this point of view the Committee consider that it is of sufficient promise to justify the expenditure necessary for further experiments as to the practicability of the process.

It is idle to suppose that we can enter on the fixed nitrogen industries to advantage unless we are prepared to pursue an active policy in regard to them.

It is satisfactory, therefore, to learn that whilst the technical staff engaged on the work of the Committee has been largely disbanded, and the temporary research laboratories restored to their original purposes, the section of the staff engaged on the synthetic ammonia problem has been taken over by the syndicate already referred to, and is continuing under them the investigation of some of the remaining problems. Moreover, although the Inventions Department of the Ministry of Munitions has ceased to exist, a small nucleus organisation has up to the present been retained, and is actively engaged in applying to the post-war situation the information and experience on the nitrogen problem collected by the Committee. I may add that at the present moment a number of important fixation schemes are in course of development, not only in the United Kingdom, but also in Egypt, South Africa, Canada, Newfoundland, the West Indies, New Zealand, Ceylon, and India, and some of these are receiving the active support of the Governments concerned.

My purpose in bringing this subject before you on the present occasion is not only to emphasise the importance of the conclusions of the Nitrogen Products Committee, but to direct attention to a wider question suggested by its inquiry. Our attitude towards the fixed nitrogen problem illustrates a defect in our attitude towards such problems generally. Where our individual interests are not affected we are prone to be indifferent to and to overlook developments in other countries which in their results may be of vital importance to us as a nation. We are thus exposed to the danger of having our economic position disturbed and our safety imperilled by the introduction of new factors of the importance, or it may be of the very existence, of which we have remained ignorant until they have made themselves felt by their consequences. Where particular industries are affected those who are immediately concerned can generally be trusted to look after their interests when they understand them. In matters which do not affect any special interest, however, but may yet be of the gravest import from the national point of view, there is no one to hold a watching brief for the nation.

While the fixed nitrogen industries were being rapily developed on the Continent the subject attracted little general attention in this country. As we had an abundant supply of ammonia and were able to import sodium nitrate at will, our interest in the new processes was purely academic. Yet our failure to realise their importance, and to grasp the larger aspects of the problems involved, nearly led to disaster.

I do not think we need take blame to ourselves for having

failed to realise in its full extent the peril to which we were exposed at the beginning of the war. That would have required gifts of imagination with which we as a nation are not usually credited. The complaint is that no consideration whatever had been given to the national aspects of the matter in relation either to peace or war conditions, and that no precautions had been taken against the more obvious dangers.

The first person in this country to direct attention prominently to the development of the fixed nitrogen industries abroad was the present Foreign Secretary of our Society. In a lecture delivered before the Pharmaceutical Society in 1910, Professor Crossley gave an account of the production of nitrogen compounds at Odda, in Norway, and pointed out the importance of the work from the national point of view. "It might naturally be expected," he said, "that the problem of the utilisation of atmospheric nitrogen should be considered as one of real and undoubted importance to the country, not only from the point of view of agriculture, but also as a means of supplying the necessary nitric acid for the manufacture of explosives. . . . Yet there do not appear to be any signs that the matter is regarded as one of national importance." Detached notices of the various methods of synthesis employed had no doubt appeared from time to time in the journals and papers at an earlier date, and in 1906 Professor Frankland, in an address to the Society of Chemical Industry at Birmingham, gave a short account of the methods that had been proposed before that date for utilising the nitrogen of the atmosphere, but Professor Crossley's lecture was, I believe, the most complete account of these new industries published in this country before the war.

In the early months of the war the nitrogen question was considered by a Committee of the Board of Agriculture, and it was soon discovered how imperfect was the information on the subject available in this country. This Committee sought the aid of the Chemical Society, and Dr. Scott, then President, was fortunate in obtaining the assistance, amongst others, of Mr. G. S. Albright, who afterwards rendered invaluable service as a member of the Nitrogen Products Committee, in preparing a Report on the subject for the Board of Agriculture. This report was placed at a later date at the disposal of the Nitrogen Products Committee, which commenced its sittings in the summer of 1916 and was engaged during the next three years in the long and elaborate inquiry which led to the conclusions we have been considering this afternoon.

In the course of its inquiry the Committee was constantly con-

fronted with the difficulty of obtaining accurate statistical and other information relating to the various industries concerned with the production of nitrogen compounds. The figures on which the Report is largely based had to be laboriously collected from many different sources. Much valuable information was obtained from the returns of the Chief Inspector of Alkali Works and other official sources, but in not a few instances figures which would have materially assisted the inquiry were altogether unprocurable. Thus, to take only one example, when considering the possibility of increasing the supply of ammonia from by-product processes, it was desirable to obtain information as to the allocation of the coal consumed in this country by different industries and classes of consumers, but no trustworthy figures were available on the subject. It is unnecessary to dwell further on the importance of pressing for the adoption of the strong recommendations which the Committee has made on this subject to the effect that annual statistics of the nitrogen and other industries of the United Kingdom should be officially collected and published.

It was, however, not statistical information only that was lacking. With the exception of the lecture I have already referred to, which was necessarily limited in its scope, we possessed at the beginning of the war no adequate account of the state of the nitrogen industries on the Continent. For that the Committee had to go to a "Report on the Utilisation of Atmospheric Nitrogen," by Thomas H. Norton, American Consul at Chemnitz. This Report was issued by the Bureau of Manufacturers of the Department of Commerce and Labour of the United States in compliance with an Act of Congress of 1911 authorising investigations of trade conditions abroad. It contains a large amount of valuable information regarding the experimental details and industrial prospects of the various fixation processes which had either achieved success or were still in the experimental stage when the Report was compiled in 1912. Although it had no special reference to the conditions in this country it was nevertheless of the greatest use to the Committee as affording a comprehensive survey of the position of the fixed nitrogen industries on the Continent shortly before the war.

Amongst the officers of his ideal State, "The New Atlantis," Bacon included twelve whose duty it was to sail into foreign countries and bring back the "books and abstracts and patterns of experiments of all other parts." These he called "Merchants of Light." We, too, have need of our Merchants of Light. Is it

too much to hope that some effective combination of the Departments concerned with the technical and scientific work of the nation may yet be devised for the purpose of keeping us in close touch with new developments abroad with which it is desirable in the interests of the State that we should be acquainted?

OBITUARY NOTICES.

SIR WILLIAM CROOKES, O.M.*

BORN JUNE 17TH, 1832; DIED APRIL 4TH, 1919.

THE author of a succession of papers published by the Royal Society and other scientific bodies extending over sixty-seven years (from 1851 to 1918), to say nothing of a number of technical treatises in the form of large volumes, must have been a man of remarkable industry as well as intellectual qualities, and those who believe in the influence of heredity will therefore be disposed to look for some indication of the ancestral origin of these qualities in the famous man who has so recently passed away.

His father, Joseph Crookes, born in 1792, the son of a small tailor in the north of England, came to London a poor boy. He was evidently a man of brain and energy, for the tailor's business he established proved so prosperous that when he died in 1884, at the age of ninety-two, he was a rich man. Joseph Crookes married on February 24th, 1831, at Aynhoe, Northamptonshire, as his second wife, Mary Scott, and from this lady he had a second family of several sons and daughters. William was her firstborn, and resembling her in feature and in disposition, it may be surmised that he derived some of his characteristics from her.

There is but little to say concerning William Crookes's early years. Improbable as it may appear, he always maintained that he remembered learning to stand and to walk. Such regular education as he received was obtained at a grammar school at Chippenham. His father wished to make him an architect, but in the end he satisfied his inclination for experimental work, already indicated at home, by entering the Royal College of Chemistry under Hofmann, the first professor, in 1848. He must have made extraordinary progress, as in 1851 his first paper appeared in three

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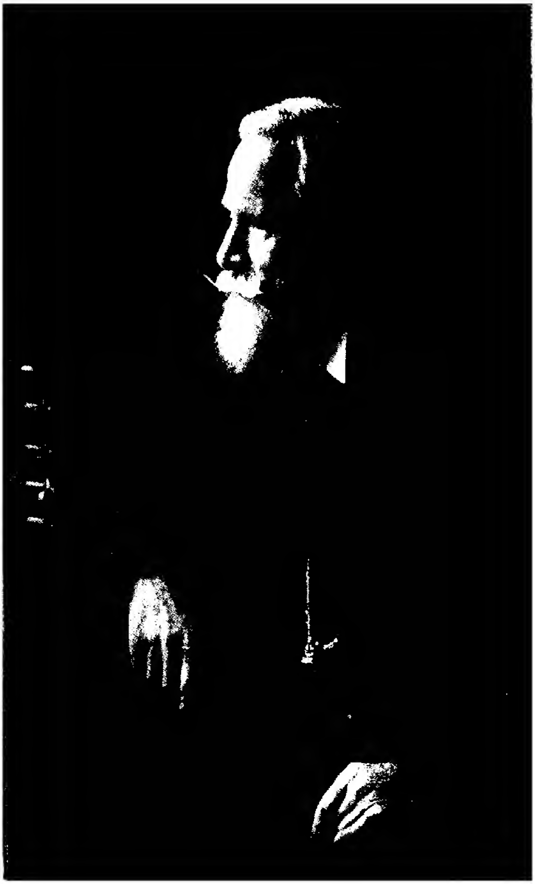


William Crookes.

[To face Trans., p. 444.

German chemical journals to which it was communicated, doubtless by Hofmann. The English version was printed in the *Quarterly Journal of the Chemical Society* (1852, **4**, 12), "On the Selenocyanides, by William Crookes, Esq., Assistant in the Royal College of Chemistry." This position as assistant he retained from 1850 to 1854. He then went to Oxford for a short time as Superintendent of the Meteorological Department at the Radcliffe Observatory, and in 1855 he became Lecturer on Chemistry at the Chester Training College.

In 1856 he married Miss Ellen Humphrey, a native of Darlington, whose acquaintance he had made some years earlier as a school friend of his cousin. They were married on April 10th, 1856, at the Parish Church of St. Pancras, Middlesex, and began housekeeping at Brompton. They removed to 20, Mornington Road, N.W., and afterwards to 7, Kensington Park Gardens in 1880, and this was their home to the end of their lives. In 1859 he brought out the first number of the *Chemical News*, of which he remained sole editor until 1906.

In the meantime he seems to have been much occupied with the study of phenomena connected with the nature and effects of light, for several papers relating to photography were published between 1853 and 1857. Soon after this, the employment of the prism in recognising and distinguishing volatile substances in flame was introduced by Bunsen and Kirchhoff, and the discovery of rubidium and cæsium in the water of the Dürkheim spring was announced by Bunsen in 1860. On applying the spectroscope to the seleniferous material from the vitriol works at Tilkerode (Harz), which had been given to him by Hofmann some years previously, and which he had used as the source of selenium in his work on the selenocyanides, Crookes observed a new green line which led him to the discovery of thallium. The first announcement of the existence of a new element appeared in the *Chemical News*, March 30th, 1861. It was originally supposed to be related to sulphur, but the discoverer soon saw fit to alter his opinion, and the specimens exhibited in the International Exhibition, 1862, and to which a medal was awarded, were labelled Thallium, *a new metallic element*. The discovery was interesting from several points of view. The use of the spectroscope was novel and the properties of the new metal were strange, exhibiting as it does the appearance and approximately the density of lead, some of its salts resembling those of lead and mercury, whilst others are perfectly similar in solubility and crystalline relations to the salts of the alkali metals. The discovery of thallium at once secured for William Crookes a recognised position in the scientific world, and in 1863 he was

elected F.R.S. Obviously the first task which lay before him was the investigation of the chemical and physical properties of the new element and its sources in nature. Among the most important of the physical constants to be determined was the atomic weight, and the remarks on the subject contained in Prof. F. W. Clarke's "Constants of Nature" (Smithsonian Institution, 1882) may properly be quoted here. "In 1873, Crookes, the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities of absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed specially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly *in vacuo*, but all were reduced to *absolute* standards, and unusually large quantities of thallium were employed in each experiment. . . . Suffice it to say that the research is a model which other chemists will do well to copy. . . . Hence, using the atomic weights and probable errors previously found for N and O, $Tl = 203{\cdot}715 \pm {\cdot}0365$. If $O = 16$, $Tl = 204{\cdot}183$. . . . Crookes himself, using 61·889 as the molecular weight of the group NO_3, gets the value $Tl = 203{\cdot}642$; the lowest value in the series being 203·628 and the highest 203·666, an extreme variation of 0·038. This is extraordinary accuracy for so high an atomic weight, at least as far as Crookes's work is concerned."

This passage illustrates the spirit which animated Crookes's work throughout. Nothing short of the highest attainable accuracy ever satisfied him.

The use of the vacuum balance, however, was attended by unexpected phenomena, which occupied his attention for many years afterwards and led to the discovery of the *radiometer* in 1875. This was described in a paper entitled "On Attraction and Repulsion resulting from Radiation," communicated to the Royal Society on March 20th, 1875. A Royal Medal was awarded to Crookes at the Anniversary Meeting in the same year. The President in presenting the medal referred to the instrument in the form in which it has been since familiar, namely, with the four-armed fly mounted on a sharp point and having the vertical disks at the ends of the arms blackened on one side. He also remarked, "it is the mystery attending this phenomenon that gives it its great importance." Great interest was manifested by many experimenters in the phenomena observed, and there were many attempts at explanation. In the end, the hypothesis put forward by Dr. G. Johnstone-Stoney, according to which the repulsion is due to the movements of the molecules of the residual gas acting

lifferentially on the two surfaces of the movable disk, was .ccepted.

In a footnote to one of his papers (*Proc. Roy. Soc.*, 1876, **25**, 308), Crookes drew attention to the properties of highly attenuated gas, and expressed the view that the phenomena indicate the existence of a fourth state of matter as far removed from the condition of gas as gas is from liquid.

In all the numerous experiments connected with this investigation, Crookes was assisted by Mr. C. H. Gimingham, whose mechanical dexterity and skill as a glass-blower were quite remarkable. Gimingham joined the Swan Electric Light Company in 1881, but unhappily died a few years later.

The phenomena exhibited by the electric discharge in rarefied gas had long been familiar, and had been studied by Plücker, by Hittorf, and other physicists. It was natural that in the examination of the properties of highly attenuated gas the phenomena exhibited by electric discharge through such media should receive Crookes's attention, and in the paper in which his first experiments in this direction were described (*Proc. Roy. Soc.*, 1879, **28**, 110), he was led to theoretical speculations on the ultra-gaseous state of matter. In this paper, the dark space which appears round the negative pole was the subject of experiment, and was found to enlarge as the exhaustion proceeds, whilst the phosphorescence excited on the glass walls of the tube diminishes and ultimately disappears. The dark region round the electrode has since been known as the *Crookes*, or *cathode dark space*. The rays from the cathode may be made to converge by the use of an aluminium cup, and the result is the production of a green phosphorescent spot on the glass; the rays, travelling in straight lines, cast a strong shadow from any object placed in their path. The rays when concentrated also develop great heat, which may rise to the melting point of platinum.

In 1880 the French Académie des Sciences awarded Crookes an extraordinary prize of 3000 francs and a gold medal in recognition of his discoveries in molecular physics and radiant matter. In the years following 1880 he continued the active investigation of the phenomena exhibited by gases in a highly attenuated state, and among other properties he studied the heat conduction and viscosities of gases in this condition. He also examined the phosphorescence exhibited by many substances when exposed to the discharge from the negative pole in a highly exhausted tube; and in the Bakerian Lecture for 1883, speaking of this discharge as "radiant matter," he considered that the particles flying from the cathode were of the dimensions of molecules.

For some years he was occupied in tracing by the spectroscope the changes noted, and he was led to attempt the separation of some of the earths, notably yttria, into the components of which they were supposed to consist, by means of a very elaborate system of chemical fractionation. The result of all this work led him to speculations as to the characters of the elements and the existence of a class of bodies which he called "meta-elements." These meta-elements he regarded as composed of atoms "almost infinitely more like each other than they are to the atoms of any other approximating element. It does not necessarily follow that the atoms shall all be absolutely alike among themselves. The atomic weight which we ascribe to yttrium therefore merely represents a mean value around which the actual weights of the individual atoms of the 'element' range within certain limits. But if my conjecture is tenable, could we separate atom from atom we should find them varying within narrow limits on each side of the mean." This view was put forward in the Presidential Address to the Chemical Society, 1888, the whole of which even now, after thirty years, would repay perusal. The possibility of the evolution of the elements from a primal elementary protyl or urstoff is a proposition which has been discussed from the most ancient times, but the chemist had little positive information as to the inter-relations among the recognised elements before the conception of the periodic law. Taking an idea from Prof. Emerson Reynolds for the diagrammatic display of the periodic relation of properties to atomic weight, Crookes produced a figure of eight curve, on which the symbols of the elements are placed at intervals so that the members of natural families fall into position vertically over one another.

On this curve the meta-elements would be ranged in groups or clusters close together. Radioactivity had not been discovered when this address was composed, but something approaching Crookes's idea has been realised in more recent times by the discovery of isotopes among the products of the disintegration of radioactive elements. For his researches on the behaviour of substances under the influence of the electric discharge in a high vacuum, with special reference to their spectroscopic behaviour, the Davy Medal was awarded to Crookes by the Royal Society in 1889.

The discovery of argon by Rayleigh and Ramsay in 1894, and of helium by Ramsay in 1895, opened a new field, and Crookes being recognised as the most experienced observer of spectra and the highest English authority in this direction, the new gases were

,t once submitted to him, and the identity of terrestrial with solar ıelium was established finally by his examination.

Soon after this time the brilliant researches of J. J. Thomson hrew an entirely new light on all the difficult spectroscopic quesions which had been so patiently and so successfully examined by Crookes. It became clear that the particles projected from the athode were much smaller than any known atoms or molecules of ordinary matter, and were, in fact, the minute bodies called electrons. On this point, Crookes in a paper on the "Stratifiations of Hydrogen" (*Proc. Roy. Soc.*, 1902, **69**, 411), expressed iimself in the following terms: "In twenty-five years one's theories nay change, although the facts on which they are based remain mmovable. What I then called 'Radiant Matter' now passes as Electrons,' a term coined by Dr. Johnstone-Stoney to represent he separate units of electricity which is as atomic as matter. What was puzzling and unexplained on the 'Radiant Matter' heory is now precise and luminous on the 'Electron' theory." And by application of this theory the stratifications of hydrogen were explained.

The discovery of radioactivity by Henri Becquerel and of radium by Madame Curie towards the end of the century naturally attracted Crookes's interest and attention. On examination of uranium salts, some specimens were found to be much more radioactive than others. It was soon found that the radioactive constituent is precipitated from a solution by ammonia, and on adding excess of the reagent, a small, insoluble, light brown precipitate is left which exhibits strong radioactive properties, whilst the uranium salt remaining is almost inactive. A year later the uranium had regained its activity. To the active substance the name uranium-X was given. Whatever be its nature, it is evident that uranium owes its usual activity to the presence of this substance which is generated from it, and the separation of which depends on the readiness with which it attaches itself to precipitates, especially ferric hydroxide, when iron is present as an impurity in the uranium compound employed as material. The year following, Crookes, continuing his observations on the emanations of radium, discovered the effects produced by the α-rays on a surface of hexagonal blende (zinc sulphide), and invented the little instrument, which he called the spinthariscope, by which the number of scintillations can be counted, each spark being produced by one α-particle.

The researches on the spectra and other characters of the rare earths occupied more than twenty years, and one result was a very

extensive study of scandium and its salts, which places it in the position of being now better known than almost any other of these difficult elements from which scandium is separated by its low atomic weight.

In 1908 Crookes drew attention to the remarkable resistance to the attack of all kinds of reagents by the metals iridium and rhodium, and in 1912 he recorded a useful series of observations on the relative volatility of metals of the platinum group. In the case of platinum at 1300°, the metal seems to volatilise *per se*, whereas the loss of weight of iridium is probably due to the formation of a volatile oxide. The spectra of elementary boron and silicon were the subjects of papers communicated to the Royal Society in 1912 and 1914.

A very valuable investigation undertaken in connexion with the Glass Workers' Cataract Committee of the Royal Society was begun in 1909. The main object was to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workpeople. This involved a study of the effects of the addition of a large number of metallic oxides to a colourless glass, specially prepared for the purpose by Mr. H. Powell, of the Whitefriars Glass Works. The problem was to prepare a glass which would cut off as much as possible of the heat radiation, and at the same time be opaque to the ultra-violet rays, whilst the colour would be scarcely noticeable when used in spectacles. In the result, a series of eighteen different recipes were provided which meet, more or less fully, the three requirements contemplated. These have been found to be, in practice, very beneficial to the workers.

We may now recall some of the subjects which at various times were studied by this untiring worker, outside the course of research which may be supposed to have represented his predilection.

It should not be forgotten that when quite a young man he was appointed by the Government to report on disinfectants and their application to the arrest of the cattle plague in 1866, and that he was responsible for the recognition of the antiseptic value of phenol or carbolic acid.

The diamond has been ever a subject of interest, not merely to the jeweller, but to the mineralogist and chemist, owing to the mystery in which, up to recent times, its origin and formation were involved. In a visit to Kimberley in 1896, Crookes spent nearly a month in the mines studying the question of the origin of the mineral, and again in 1905, on the occasion of the visit of the British Association, he pursued the same inquiry. In 1893 the late Prof. Moissan demonstrated the production of diamonds by crystallisation of carbon from molten iron under pressure, and

Crookes showed that the residue of cordite exploded in a closed steel cylinder contains crystalline particles possessing the form of the diamond. He published an interesting little book on diamonds in 1909.

Another subject in connexion with which he did good service was the importance of producing and applying to the land much larger quantities of nitrogen in the form of nitrate in order to increase the supply of wheat. "The Wheat Problem" was one theme of his Presidential Address to the British Association at the meeting at Bristol in 1898, and his views on the subject were embodied in a volume published a year later, in which he was able to reply to the various critics who in the meantime had questioned some of his conclusions. Though, doubtless, some of his most startling statements admit of modification, the problem still remains a topic of supreme interest to the agriculturist and to the world at large.

It would be almost impossible to enumerate all the various directions in which Sir William Crookes (he received the honour of knighthood in 1897) occupied himself in connexion with problems of public interest or as expert adviser to the Government, but, in passing, may be mentioned his work on the disposal of town sewage, his reports on the composition and quality of daily samples of the water supplied to London from 1880 to 1906, and his services as Consulting Expert on the Ordnance Board from 1907 onwards during the period of the war. Nor should it be forgotten that the office of President is in many learned societies no sinecure. In presiding over the Chemical Society (1887–1889), the Institution of Electrical Engineers (1890–1894), the British Association (1898), the Society of Chemical Industry (1913), and, finally, the Royal Society (1913–14–15), Sir William paid close attention to all the multifarious details of the business of each society. He also served as Honorary Secretary to the Royal Institution from 1900 to 1913, and as Foreign Secretary to the Royal Society from 1908 to 1912. Every man of science among his contemporaries will be ready to affirm, therefore, that the numerous honours which were showered on Crookes by the most distinguished academies and universities in the world were well earned and very fittingly conferred. He received from the Royal Society the Royal, the Davy, and the Copley Medals, and from the Royal Society of Arts the Albert Medal, and finally, in 1910, the Order of Merit was conferred on him by the King.

Crookes's whole scientific career is interesting, apart from the value of his discoveries, as illustrating the fact that to a man of genius the character of his early education has but little influence

on his achievements. As mentioned already, he left school at the early age of fifteen, and at once specialised in a single branch of science under a teacher eminent in his own line, but from whom the young student seems to have derived little but the advantage of example, for the subjects to which Hofmann devoted his energies appear to have had but little attraction for Crookes. Unlike W. H. Perkin, who also entered the college at about the age of fifteen with equally imperfect general education, he never seems to have been attracted by organic chemistry, and to the end of his life remained practically ignorant of this branch of science. The genius displayed by Crookes was, however, accompanied by unusual independence of character, which was displayed in a variety of ways, not only in the course taken by his own researches, but by his attitude toward the statements and pretensions of others. Nothing seemed too improbable to escape his attention, and of this the time and trouble he was tempted to expend on the pretended transmutation of silver into gold some twenty years ago is a sufficient illustration. The same liberality of spirit made him very tolerant, and perhaps not always sufficiently critical, in regard to articles in his paper, the *Chemical News*.

Here we must add that no account of William Crookes's life as a scientific man would be complete, and less than justice would be done to his personal character and independence of spirit, if all reference were omitted to the investigations in which, early in his career, he became involved concerning the phenomena of so-called "Spiritualism." The *Quarterly Journal of Science* for July, 1870 contains an article under the title, "Experimental Investigation of a New Force," in which Crookes describes experiments undertaken with Mr. D. D. Home, a "medium" well known to the public at that time. At one of the earlier *séances* the experiments were made in the presence of Dr. Huggins (afterwards Sir William Huggins, President of the Royal Society), Serjeant Cox, proprietor and conductor of the *Law Times* and *Recorder of Portsmouth*, one of Crookes's brothers, and his chemical assistant. Later, in January, 1874, the same journal published "Notes of an Enquiry into the Phenomena called Spiritual during the years 1870-73," with the signature William Crookes.

Anyone who has read these articles can realise the shock which was experienced by the scientific world on learning the character of the statements contained in them. Here was a well-known man of science, a Fellow of the Royal Society, the discoverer of thallium, with which and with its salts chemists had had time to become perfectly familiar, asserting in the most formal manner that in his presence things had been seen and done which everyone would

regard as contrary to well-established natural law and to all ordinary experience.

It is perhaps not surprising that Crookes was publicly attacked in a violent manner, but he was able to show that many misrepresentations and misstatements were made which everyone must now perceive were wholly unjustifiable. The story of his experiences as told by him is supported by evidence which would be accepted as conclusive if these statements related to any scientific work or to any ordinary occurrence. Crookes himself never withdrew or altered his statements concerning the phenomena he had witnessed, and in his Presidential Address to the meeting of the British Association at Bristol, so late as 1898, he reiterated his conviction as to their reality. This conviction he retained to the end of his life. He was President of the Society for Psychical Research in 1897. His view, if he really had a settled opinion, as to the explanation of these strange phenomena cannot be given in his own words, but the view of Mr. Serjeant Cox on the theory of what he called psychic force is given very clearly at the end of these "Notes," and it appears probable from the prominence given to this exposition that it represents very nearly the opinion of Crookes himself. Perhaps the last few lines are sufficient to quote in this place, as probably views may have changed during the forty-five years since they were written. The passage is as follows: "The difference between the advocates of psychic force and the Spiritualists consists in this—that we contend that there is as yet insufficient proof of any other directing agent than the Intelligence of the Medium, and no proof whatever of the agency of the Spirits of the Dead; while the Spiritualists hold it as a faith, not demanding further proof, that the Spirits of the Dead are the sole agents in the production of all the phenomena. Thus the controversy resolves itself into a pure question of *fact*; only to be determined by a laborious and long-continued series of experiments and an extensive collection of psychological facts."

It is unnecessary to pursue the subject further, but as Crookes made no secret of his views, and his credibility in regard to all other questions, scientific or otherwise, has never been impugned, his biographer would not be justified in doing more or less than to place on record such statements as appear to represent fairly the position he had assumed, and certainly no biographer would be expected to pronounce any opinion other than that which he believes to have been entertained by the subject of his notice.

By the death of Sir William Crookes on April 4th, 1919, the world lost a great scientific pioneer. His age was far advanced, and the loss of his wife some three years earlier had been a severe

blow, from which he never completely recovered, so that when in January last year his friends learned of his increasing weakness, it was with the sad conviction that the end was not far off. The touching dedication prefixed to his little book on Diamonds was an indication of the domestic happiness which throughout accompanied his long and active career.

W. A. T.

THOMAS FAIRLEY.

BORN 1843; DIED FEBRUARY 21ST, 1919.

THOMAS FAIRLEY, who died on February 21st, 1919, at the age of seventy-six, had been a Fellow of the Society since 1865.

He was born in Glasgow, and received his school education in the Free Church Training College of Edinburgh, where, as is indicated by still extant evidence, he distinguished himself in classical study as well as in mathematics and physical science. He had begun to amuse himself with chemical experiments in early childhood, and his early acquired chemical taste led him, on leaving school, to become first a student with, and subsequently an assistant to, Lyon Playfair at Edinburgh University. After some time spent thus he migrated to Leeds to become a teacher in the Grammar School there and lecturer in chemistry in the local School of Medicine. At the same time he began to practice as a chemical consultant, and when the Sale of Food and Drugs Act of 1873 came into operation, he was appointed Public Analyst for Leeds and the North Riding of Yorkshire. At a later date he became official Agricultural Analyst under the Fertilisers and Feedings Stuffs Act for both the North and West Riding, having for many years previously acted as consulting chemist to the Yorkshire Agricultural Society.

He had acted both as Treasurer and as Chairman of the Yorkshire section of the Society of Chemical Industry, of which society he also became Vice-President; also as President of the Leeds Naturalists' Field Association, and as Chairman of the Leeds Institute of Science, Art, and Literature, and while holding this office he was elected Chairman of the Council of the Association of Technical Institutions of Great Britain and Ireland in 1908.

He served a full term as examiner during the earlier days of the Institute of Chemistry, and became a Vice-President of that body, in the welfare of which he always took an active and cordial

interest, and he was President of the Society of Public Analysts in 1903 and 1904.

Fairley's earliest contribution to chemical literature was a paper on "The Action of Hydrogen on Organic Polycyanides" (*Journ. Chem. Soc.*, 1864, **17**, 362). This paper incidentally records the first successful attempt at the synthesis of cyanoform, which the author prepared by heating together chloroform, potassium cyanide, and alcohol at 100° under pressure. Fairley's experiment appears to have been successfully repeated seven years later by Pfankuch (*J. pr. Chem.*, 1871, [ii], **4**, 38). Further contributions to the *Journal* were: "Analysis of Water from the 'Old Crescent Well,' Harrogate" (1875), "A New Oxide and Acid of Uranium" (1876), and "Study of Hydrogen Dioxide and of Certain Peroxides, including Experiments to determine the Heat of Formation of the Oxygen Molecule" (1877).

To the *Transactions* of the British Association he contributed papers on: "Organic Cyanides" (1865 and 1868), "The Use of Platinum Black in the Preparation of Ethylene Diamine" (1868), "Preparation of Olefiant Gas" (1868), "Preparation of Cyanogen and Hydriodate of Cyanogen" (1870), "Use of Platinised Charcoal in the Hydrogenation of Cyanogen" (1870), and "The Distillation of Sulphuric Acid" (1870).

To the *Journal of the Society of Chemical Industry* he contributed: "Note on the Detection of Certain Adulterations in Dyestuffs" (1886), "On the Estimation of Sulphur and Impurities in Coal Gas" (1886), "On the Various Forms of Filter-pumps or Water-jet Aspirators" (1887), "On the Impurities of Coal Gas" (1892), "Note on the Durabilities of Platinum–Iridium Vessels in Laboratory Use" (1896), and "The Manufacture of Ammonium Nitrate by Double Decomposition" (1897).

Published in the *Analyst* were the following papers: "Note on the Estimation of Chlorine in Water" (1893), "Arsenic Estimation relating to Malt-kilns" (1901), "Notes on the History of Distilled Spirits, especially Whisky and Brandy" (1905), and "On the Phosphates in Certain Vinegars, and the Materials used in their Manufacture" (1909). The paper on the distillation of spirits was one recording the results of interesting antiquarian research into the early antecedents of an industry which at about that time was the subject of much legal contention and of a monumental official investigation.

A paper on "The Water Supplies of Yorkshire" was contributed in 1898 to the *Journal of the Federated Institute of Brewing*.

Various other notes from Fairley's pen appeared at various times in the *Chemical News* and *Pharmaceutical Journal*, and he was

one of the contributors on subjects connected with laboratory apparatus to Thorpe's "Dictionary of Applied Chemistry."

As gas examiner to the City of Leeds, he became interested in questions relating to the manufacture and purification of coal-gas, to which he devoted a good deal of practical attention.

His health and activity were well maintained until 1911, when he had an illness from the effects of which he never completely recovered.

B. DYER.

WALTER WILLIAM FISHER.

BORN 1842; DIED FEBRUARY 7TH, 1920.

WALTER WILLIAM FISHER, Aldrichian Demonstrator in the University, Oxford, who died on February 7th, in his seventy-eighth year, had been a member of the Society since 1872.

He was educated at Worcester and Merton Colleges, Oxford, where he took a first class in chemistry in the School of Natural Science in 1870, and in the following year also succeeded in taking a class in "Greats," and he was shortly afterwards elected a Fellow of Corpus Christi College. He became chemical assistant to the late Vernon Harcourt, and in January, 1872, was appointed by the late Sir Benjamin Brodie as University Aldrichian Demonstrator in Chemistry, a post which he continued to hold until his death. For six years, from 1874, he was also lecturer in chemistry at Balliol, and he served from time to time as a public examiner for the University. He also acted as examiner to the Institute of Chemistry from 1903 to 1907, and served for several periods as a Member of Council of that body.

To the *Transactions* of the Chemical Society Fisher contributed papers on "Manganese Tetrachloride" (1878) and "Lead Tetrachloride" (1878), and to the *Proceedings* in 1892 a paper on "Anhydrous Oxalic Acid." He was a keen field botanist and a good geologist, and took a large interest in the subject of the composition of well waters from various water-bearing strata, several papers from him on this subject having appeared from time to time in the *Analyst*, notably one on "Alkaline Waters from the Chalk" (*Analyst*, 1901) and one on "Alkaline Waters from the Lower Greensand" (*Analyst*, 1902).

He had an extensive professional practice as a water analyst and as Public Analyst under the Sale of Food and Drugs Act, having been for nearly forty years Public Analyst for the counties

of Oxford, Berks, and Bucks, and also for the City of Oxford and for boroughs within the area of the aforesaid counties.

He was a man of fine physique, and in his early days was distinguished as a college oarsman, as well as on the running path; whilst during eleven years' volunteer service in the 1st Surrey Rifles in his early days he won numerous shooting prizes.

His life was lived mainly within his university, and he was less well known in the general chemical circle than were many of his contemporaries. But by those who came within the range of his genial personal friendship he was much loved and will be sadly missed.

B. Dyer.

ANTOINE PAUL NICOLAS FRANCHIMONT.

Born May 10th, 1844; Died July 2nd, 1919.

Antoine Paul Nicolas Franchimont, Professor of Organic Chemistry in the University of Leiden and an Honorary Foreign Member of the Chemical Society, was born at Leiden on May 10th, 1844. He came of an old French refugee family, who after 1687 migrated to Holland from the neighbourhood of Spa, where the ruins of their ancestral castle, "The Franchimont," still exist. His father was the minister of the French Church at Leiden, and had married the daughter of a Dutch pastor. The young Antoine was a weak, fragile child, too frail to be sent to school in his early years, and hence owed his primary education mainly to his father. In his later boyhood he attended the Lyceum, the principal public school of Leiden. It was intended that he should become an apothecary, and he gained his diploma in 1864, but after a few years' service he relinquished that occupation and entered the University of Leiden as a student of chemistry, obtaining his doctorate in 1871 for a thesis on "Contributions to the Knowledge of the Origin and Chemical Constitution of the so-called Turpentine Resins." His first teacher was Van der Boon Mesch, a chemist of the old school, whose contributions to experimental chemistry were almost wholly concerned with mineralogical or geochemical subjects. Organic chemistry was scarcely studied at Leiden in those days.

Accordingly, Franchimont proceeded to Bonn, where his zeal and ability were quickly recognised by Kekulé, to whom he became private assistant. He remained at Bonn about eighteen months,

and thence went to Paris to work under Wurtz. Here he gained the friendship of Friedel and Le Bel. In 1873 he returned to Holland, and was attached, as teacher of chemistry, to the school of agriculture at Wageningen, but in the following year was called to Leiden to fill the newly-created chair of organic chemistry, established on the retirement of Van der Boon Mesch, a position which he continued to occupy until his retirement on reaching the age-limit in May, 1914.

Franchimont's association with Kekulé may be said to have influenced his whole career. It had a no less marked effect on the status and development of organic chemistry in Holland. He entered on his professorship at a momentous epoch in the history of chemistry, and he was not insensible to the opportunity which the times had brought him. He came to be regarded as a missionary in the new movement which Kekulé initiated, and he made Leiden the most progressive school of modern chemistry in the Netherlands. His success may be judged from the number and variety of his published contributions to its chemical literature, and from the character of the men who were attracted by his teaching—among them may be named Lobry de Bruyn, van Romburgh, Holleman, Klobbie, van Erp, Backer, and others who have occupied teaching positions in Holland or who have associated themselves with its industrial development.

Franchimont was an excellent teacher and an admirable lecturer, enthusiastic and inspiring. His lectures were always carefully prepared according to a well-considered scheme, and he spared no effort to make them interesting and profitable. Advanced students could always learn something from his methods, from the originality of his views and the wide range of his knowledge; whilst beginners, although they might at times be perplexed by the rapidity of his utterance, and his quick-change blackboard practice, chalk in one hand and sponge in the other, could not fail to be impressed by his evident mastery of his subject.

It was, however, in the laboratory that his influence was mainly felt. He seemed to take a special interest in the work of each pupil, and regularly went his rounds twice a day. Like Kekulé, for whose methods he always expressed great admiration, he attached much importance to cleanliness and neatness of manipulation, qualities which characterised his own work. The Leiden laboratory, when he retired in 1914, showed few signs of wear, although some hundreds of students had passed through it since its opening in 1901.

His activities were, however, affected in the outset by various adverse circumstances, and it says much for his energy, persever-

ance, and patience that he should have been able to accomplish so much. During the greater part of his career at Leiden he was hampered by the conditions under which he had to work: the old laboratory was small and poorly furnished and lacked the structural fittings and appliances of modern methods of research. Holland at that period had relatively few openings for a career in chemistry, and the number of those who occupied themselves in the pursuit of that science as a profession was consequently small. Hence there was little public pressure on the Government to build and equip chemical laboratories of a type demanded by the times. As regards Leiden, the State seemed content for years to allow it to live on the traditions of Boerhaave. Franchimont must frequently have sighed for some of the arrangements he had learned to know and to appreciate in the spacious temple, which, under the inspiration and guidance of Hofmann, had been erected in the Poppelsdorfer Alleé in Bonn. But everything comes to him who waits. After many and long delays his hopes and wishes were gratified, and, thanks to his industry and zeal, Leiden now possesses an admirably arranged laboratory for the study of organic chemistry. In its planning and equipment Franchimont took the keenest interest, sparing no trouble to make himself acquainted with every detail that would contribute to its utility and convenience. The writer recalls the lively pleasure with which he inspected the buildings of the then recently erected Government laboratories in Clement's Inn Passage, and the quick appreciation with which he noted any contrivance that would facilitate the operations of analytical chemistry.

When the new Leiden laboratory was opened Franchimont had occupied his chair for twenty-seven years, and much of his intellectual vigour and creative power were spent. He used to lament that for him it had come too late, but to the last he continued to regard it with pride and affection. He could have desired no more appropriate monument by which to perpetuate the memory of his long and fruitful association with the famous old University.

On the twenty-fifth anniversary of his election to his professorship his friends presented him with his portrait, painted by the distinguished Dutch artist, Therese Schwartze, which is ultimately to pass into the possession of the University. On the occasion of the fortieth anniversary, a week before his seventieth birthday, a relief portrait in bronze by Toon Dupuis was offered to the new laboratory to be affixed to the wall of the entrance vestibule.

Franchimont, on his retirement, mainly occupied himself with his duties as one of the editors of the *Recueil des Travaux Chimiques des Pays-Bas et de la Belgique*, with which he had been

connected since 1882, and in which his own contributions to science for the most part appeared.

Although towards the end of his days his physical strength was greatly impaired, and he suffered acutely at times from the effects of the painful malady to which he ultimately succumbed, his mind continued active and alert to the last, and he read and corrected proof-sheets to within a week of his death on July 2nd, 1919.

A man of simple tastes and habits, happy in his relations with his colleagues and pupils, and in his home life—he had married Miss Cornelia van Batenburg, a member of an old Gelderland family, in 1880—his interests were wholly centred in the duties and responsibilities of his office. He lived the serene, contemplative existence of the philosophic student, devoting his life to the elucidation of a special class of phenomena. The character of his studies was, of course, mainly determined by the requirements of his professorship, but his knowledge as a chemist was by no means limited to his own department. He was an omnivorous reader, and followed the development of every section with equal interest. He had a sound judgment, a strong logical faculty, and keen intuitive power—qualities which made him an admirable editor and a capable and judicious critic. He was blessed with a happy temperament and a genial manner, and had the saving grace of humour. Although absorbed in his work, and apt to resent interruptions to it by the routine calls of academic trivialities, he was in no sense a recluse, but when the occasion demanded took his full share in the management of university affairs.

Franchimont's first published paper on "Turpentine Resins" appeared in the *Archives Néerlandaises* for 1871, and was quickly followed by communications on heptylic acid and heptyl alcohol. With Kekulé he discovered triphenylamine, and he detected the formation of anthraquinone in the preparation of benzophenone. These, it is believed, were the only papers on aromatic chemistry with which he was directly concerned. During his stay in Bonn he also worked with Zincke on the aliphatic derivatives from Heracleum oil—a subject which had already engaged his attention before his visit to Germany. Indeed, he seemed almost exclusively attracted to the chemistry of aliphatic compounds, and practically the greater part of his memoirs, as well as those he published in collaboration with his pupils, deal with this class of substances. During the forty years of his activity at Leiden upwards of one hundred contributions to the periodical literature of chemistry emanated from his laboratory, apart from the many graduation theses which he may have inspired. Considerations of space prevent any detailed examination of this mass of work, but certain

papers of special significance require notice. Among them is the memoir on the "Acetylisation of Glucose" (1879), leading to the isolation of the penta-acetate, which subsequently played so important a part in Emil Fischer's researches on the isomeric derivatives of glucose. Next is the paper on the "Acetylisation of Cellulose" (1879–1881), when he prepared three acetates, one of which was afterwards identified by Skraup and König, in 1901, as the octa-acetate of cellobiose. From these researches originated the methods of acetylation now in common use, thereby laying the foundations of an important technical industry.

Franchimont's name is, however, principally associated with the study of the nitroamino-compounds—a class of substances with which the Leiden laboratory is identified. In collaboration with van Romburgh he investigated the action of nitric acid on dimethylaniline, which resulted in the discovery of trinitrophenylmethylnitroamine—the "tetryl" of these later days. Franchimont also prepared dinitrodimethyloxamide and dimethylnitroamine.

With Klobbie (1888) he obtained methylnitroamine, an acid substance isomeric with Frankland's dinitromethylic acid, by the action of ammonia on methyl nitrourethane.

With his pupil, van Erp, he found (1894) that alkylation of the monoalkylnitroamines gives not only the dialkylnitroamines, but also isomeric forms, which may be regarded as oxygen esters—one of the first of the illustrations of isomerism to be studied by Hantzsch with his theory of pseudo-acids.

A complete list of Franchimont's papers, together with the titles of the various graduation theses which originated in his laboratory, has been compiled by his pupil, Professor Backer, and is published in the *Chemisch Weekblad*, 1914, No. 18.

Franchimont was also the author of several text-books on organic chemistry which had a considerable measure of popularity in their day, but have now been largely superseded by more modern works. Compilation of literature of this kind was not a congenial task to a mind of his originality.

Franchimont was an Officer of the Order of the Dutch Lion, and of the Legion of Honour, and a member of the Dutch Academy of Sciences of Amsterdam. He was elected an Honorary Foreign Member of the Chemical Society in January, 1898.

My acknowledgments and thanks are due to Miss J. J. P. Brants, a niece of the late Professor Franchimont, and also to Professor Backer, of the University of Groningen, for the information and assistance they have afforded me in the preparation of this notice.

T. E. THORPE.

HAROLD CECIL GREENWOOD.

BORN MAY 3RD, 1887; DIED NOVEMBER 4TH, 1919.

HAROLD CECIL GREENWOOD, O.B.E., D.Sc., F.I.C., was born at Edenfield, near Manchester, on May 3rd, 1887, and was educated at the Grammar School, Bury. He entered for his Science Course at Manchester University at an early age, and graduated as B.Sc. with first-class honours in chemistry in 1907. He obtained in succession the Mercer Scholarship, the Beyer Fellowship, and an 1851 Exhibition Scholarship. During this period the Electrochemical Department of the University was constituted under Dr. R. S. Hutton, and Greenwood became one of his most enthusiastic students. He carried out a series of important researches on the production of ferro-alloys, the reduction of refractory oxides, and on the boiling points of metals, first at atmospheric pressure, afterwards studying the effect of reduction of pressure on the boiling point. Later he employed some of the pressure furnaces designed by Dr. J. E. Petavel for further study under increased pressure. His researches in this field furnish the accepted data for most of the substances he studied. On obtaining the 1851 Scholarship, Greenwood proceeded to Karlsruhe, where he worked for a period with Professor Haber. Following up the earlier work of Haber and Le Rossignol, Greenwood's research on the synthetic production of ammonia by means of the uranium carbide catalyst, and his study of the details of this reaction under varying conditions of flow rate, temperature, pressure, etc., probably marked the stage at which it was first realised that a successful technical process might be founded on it. The Badische Company had already begun to take an interest in the developments at Karlsruhe and to help to finance the expenses of the research; therefore when, after six months' work, the time arrived for a report of progress to be furnished by Greenwood to the Commissioners of the 1851 Exhibition, he was obliged to go before some of the Badische directors to be catechised as to what use would be made in England of the report. Would it fall into the hands of Sir William Ramsay? The publication of this research, and of a number of others carried out by Haber's co-workers at Karlsruhe about the same period, was held over until after the outbreak of war, by which time the technical success of the synthetic ammonia process had been assured.

Greenwood returned to England in the year 1910, and worked for some time in the Heat Division of the National Physical

Laboratory on the specific heat of metals at high temperatures, elaborating the method formerly employed by Harker in his determination of the specific heat of iron. He obtained the D.Sc. from Manchester University in 1912, and became a Fellow of the Chemical Society in the same year. He was subsequently appointed Research Chemist to the firm of William Hutton and Sons, Ltd., of Sheffield, where he investigated problems cognate to the electroplating industry.

Early in 1916, when the submarine campaign had begun to cause anxiety as to the country's supplies of sodium nitrate from Chile, the Faraday Society appointed a small committee to prepare a memorandum on the question of nitrogen fixation for submission to the Ministry of Munitions. Of this committee Greenwood subsequently became a member. After a number of preliminary conferences, the Nitrogen Products Committee of the Ministry was constituted, and among its other activities it was decided to commence experimental work on certain problems relating to fixation. Although at that time it was not anticipated that there would be any shortage of supplies of ammonia, yet it was deemed desirable, in view of the suitability of the synthetic ammonia process for the needs of the country, that an experimental study of it should be made forthwith, so that the required information should be available if necessary. Greenwood at the time was serving as a technical officer in the R.N.V.R., but in view of his previous experience his services were requisitioned at the writer's suggestion, and he became the head of the Synthetic Ammonia Section of the Research Laboratory established by the Munitions Inventions Department. This was located in premises placed at the disposal of the Government in the new Ramsay building at University College, chiefly through the instrumentality of the Provost and Professor Donnan. In the early stages of the work there were many difficulties with which to contend, but in his section a considerable measure of success was quickly achieved by Greenwood and his collaborators. After a year's experimentation, it was decided by the committee to establish a technical plant on a moderate scale, since by means of this plant it was hoped that a study of the chemical engineering problems could follow on that already made of the pure chemistry of the reactions involved.

Early in 1918, however, the engineers of the Explosives Department decided that the progress made justified them in proceeding with a scheme for the erection of a large works for the manufacture of synthetic ammonium nitrate, and a site on the River Tees was ultimately chosen, and building operations were begun. At the time of the Armistice, however, the factory was far from

complete, and since then arrangements have been made for its transfer from Government ownership to private enterprise. In the following autumn Greenwood was taken over into the service of the Syndicate which was to assume control of the new development. He had been engaged only a few weeks on his new duties as their chief research chemist when he was suddenly taken ill. After a few days' illness he died from blood poisoning at Winnington Hall, Northwich, on November 4th, 1919, at the early age of thirty-two years.

Dr. Greenwood married, in 1913, Miss M. G. Horsfall, who, herself a graduate in science, was able to render her husband valuable assistance in his work. He leaves no family.

Just before his death he had completed for press an important work on "Industrial Gases" for Dr. Samuel Rideal's series, which has since been published.

Although of a rather shy and retiring disposition, the reverse of dogmatic, and not excelling as an expositor, Greenwood possessed the true research instinct, and had a genial and attractive personality. He won the esteem of all who worked with him. His output of research was one of which many a much older man would have been proud; by his death, experimental applied chemistry suffers a severe loss.

J. A. Harker.

CHARLES EDWARD GROVES.

Born March 4th, 1841; Died February 1st, 1920.

Though during the last twenty years of his life the figure of C. E. Groves was less familiar than formerly to the Fellows of the Chemical Society, no one was better known and esteemed during the long period in which he held office as Editor of the *Journal*.

Groves was born at Highgate on March 4th, 1841, but while still a young child his parents removed to Kennington, and in that neighbourhood he remained until the end of his life. He was educated at Brixton College School, and subsequently entered the Royal College of Chemistry under Hofmann, the first professor. In October, 1862, he became chief private assistant to Dr. John Stenhouse, F.R.S., who had a laboratory for research in Rodney Street, Pentonville. This was an almost unique establishment. Stenhouse had been for some years lecturer on chemistry at St. Bartholomew's Medical School, but about the year 1856 he had

been disabled by a paralytic stroke, from which he partly, but never wholly, recovered. His interest in chemical investigation prompted him, notwithstanding his crippled condition, to resume his researches into the nature of the crystalline constituents of lichens and other vegetable materials, and he found premises to suit his purpose in an old house to which was attached the outbuildings of an abandoned artificial flower factory. Here early in 1860 he established himself with E. J. Mills (afterwards professor in Glasgow) as his scientific assistant. Mills was succeeded in Stenhouse's laboratory by C. E. Groves, together with W. A. Tilden as junior. When the latter left, for a post at the Pharmaceutical Society, he was succeeded by R. Meldola (afterwards President of the Chemical Society) and T. Bolas. The little laboratory was always busy, and Groves remained in command until the death of Stenhouse in 1880. During the later years of this association the papers resulting from the work done were published in the joint names of Stenhouse and Groves. Both were men of earnest religious convictions, and "the Doctor," who could only sit and watch operations, was much disposed to talk during work, which was not unfrequently interrupted by controversy on subjects connected with their respective religious views, Stenhouse being a Presbyterian and great admirer of the famous preacher Charles Spurgeon, while Groves, as a high churchman, stood up for the episcopal establishment.

In 1865 Stenhouse succeeded Hofmann as one of the external Assayers to the Royal Mint, and held the office until it was abolished by Mr. Robert Lowe in 1870. Stenhouse, of course, was incapable of any sort of manipulation, and the work was done by Groves with the aid of a technical assistant.

In 1877, when the Institute of Chemistry was founded, Groves took an active part in the movement and was appointed Secretary; from 1887 to 1892 he was also Registrar. He was connected with the *Journal of the Chemical Society* from 1878, first as Sub-Editor and in 1884 as Editor, in succession to Mr. Henry Watts. This office he resigned in 1899. Soon after Dr. Stenhouse's death in 1880 Groves was appointed Lecturer on Chemistry and Dental Metallurgy in the Medical School at Guy's Hospital, retiring in 1901. For more than twenty years he was also consulting chemist to the Thames Conservancy Board, and gave up this work in 1909. For only a few years later he was able to sustain his interest in scientific work, but failing health compelled him to retire from active life or study, and he died at his house on Kennington Green, February 1st, 1920.

Groves became a Fellow of the Royal Society in 1883.

Groves was a good manipulator and skilful analyst. His familiarity with several languages and his extensive knowledge of physical and chemical science were valuable qualifications for the post of Editor, though he may perhaps be remembered for certain peculiarities of phraseology in English on which he insisted and which sometimes brought him into conflict with less scrupulous contributors to the pages of the *Journal.*

In early life he was a great walker, and though in frame very spare he was both muscular and active. Though not addicted to games, he found his recreation in mountaineering, and for many years his summer vacations were spent in Switzerland. He will be remembered by many among the older members of the Alpine Club.

W. A. T.

JOHN HOLMES.

BORN JANUARY 15TH, 1871; DIED OCTOBER 1ST, 1919.

JOHN HOLMES, who died on October 1st, 1919, after a short illness, at the age of forty-eight, received his early education at Giggleswick School. Entering the Royal College of Science as a revenue student in 1894, he passed with much credit through the prescribed course of studies, and was afterwards employed in the Government Laboratory--first as a chemical assistant, and subsequently as a member of the permanent analytical staff. During the early part of this period he carried out several investigations in collaboration with Sir Edward Thorpe, including one on the occurrence of paraffins in the leaf of tobacco (T., 1901, **79**, 982), and one on the constitution of the fat present in the yolk of eggs. Later, he worked out the now well-known "Thorpe and Holmes" method for the quantitative estimation of methyl alcohol in mixture with ethyl alcohol by oxidation of the former to carbon dioxide. Much of his work at this period was concerned with questions relating to alcohol, and in the laborious task of compiling a series of revised alcoholometric tables, published officially in 1912, Holmes had a prominent part. A process for the accurate determination of ethyl alcohol in commercial fusel oil is also due to him.

Problems in physical chemistry, especially those concerned with the theory of solutions and the intermiscibility of liquids, had always a great interest for Holmes. A series of papers by him on these subjects has appeared in the Society's *Transactions* (1907, 1908, 1909, 1913, 1915, and 1918). Although lucid exposition was

not the author's *forte*, the experimental results disclosed in some of these papers are quite noteworthy; and it might, perhaps, well repay some physical chemist, who is not too much trammelled by accepted theories, to look carefully into these researches, even if it should turn out that he is not in agreement with the author's theoretical explanations of the results obtained.

Holmes was a man of equable temper and kindly disposition. In his younger days he was an excellent all-round man at sports, and could point with pardonable pride to a goodly collection of trophies carried off in athletic contests. Scientifically, his bent was distinctly that of the investigator. He was never so happy as when, the day's work done, he could devote his spare hours to following up in the laboratory some new clue revealed by previous experiments, or some fresh line of thought which his reading had suggested. In his modest way he was veritably of those "who seek knowledge simply because they crave for it"; and to a Fellow of the Chemical Society no better tribute than this can be paid.

C. Simmonds.

SIR BOVERTON REDWOOD, BART.

Born April 26th, 1846; Died June 4th, 1919.

Sir Boverton Redwood, who died on June 4th, 1919, after a brief illness, was the eldest son of Dr. Theophilus Redwood, of Boverton, Glamorganshire, who was for forty years Professor of Pharmacy in the Pharmaceutical Society at Bloomsbury Square. It was quite natural, therefore, that Boverton Redwood chose the study of chemistry as a profession.

Boverton Redwood was born near to the scene of his father's activities at 19 Montague Street, Russell Square, on April 26th, 1846. He studied at University College School, where he showed his inclination for the pursuit of science. On leaving University College he entered his father's laboratory, where he received his early instructions in practical chemistry. In 1866, at the age of twenty, he was elected a Fellow of the Chemical Society and twice served on the Council.

In 1869 he was appointed Secretary and Chemist to the Petroleum Association, and this caused him to turn his attention to the study of mineral oils, a subject at that time quite in its infancy, the chemical side of which had scarcely been touched. In fact, the American oil had only recently been struck, and at that

time the chief source of mineral oil was the distillation of shale by Young's process. In a short time he became the leading expert on the subject of mineral oils, and kept pace with its rapid developments until the day of his death.

His earliest recorded work in connexion with mineral oils had to deal with the testing of the flash point. In 1872 he gave evidence before a select committee of the House of Lords on the subject, and in 1877, in conjunction with Sir Frederick Abel, he carried out researches which resulted in standardising the method of testing for flash points and the establishment of the Abel apparatus as the legal basis for testing flash points of low flash oils. In the same year he visited the United States to carry on further investigations on the subject.

In 1881 he studied the effect of barometric pressure on the gaseous constituents dissolved in oils. These tests were carried out at various heights in the Alps and in a pressure chamber at Berlin. Following up this line of investigation he visited India and carried out further tests as to the influence of climate. As a result of this work he—jointly with Sir Frederick Abel and Dr. Kellner—advised the Government of India in amending the Petroleum Act.

He travelled considerably and examined petroleum wells in all parts of the world, and by this means obtained a first-hand knowledge of the oil industry and followed its developments.

In 1886 he turned his attention to the viscosity of lubricating oils, and designed the Redwood viscosimeter, which has become the standard instrument in the British oil industry. Recently he devised a modified form for use with heavy fuel oils, and this is now known as the Admiralty standard.

In 1892 Redwood visited Egypt in reference to the transport of oil in bulk through the Suez Canal. In 1894 the Institution of Civil Engineers awarded him the Telford premium for his work in reference to the accumulation of petroleum vapour in tanks and difficultly accessible parts of ships carrying petroleum. He designed a special apparatus for testing for the presence of such vapours. About the same time, in conjunction with his brother Robert Redwood, and Mr. H. Barringer, he invented the Redwood water-finder, an instrument for determining the amount of water which has collected beneath the oil in tanks.

Redwood was one of the first to attempt the cracking of oils for the production of lighter oils from heavy residues. In this connexion he and Sir James Dewar patented a process in 1889 for distilling and condensing oils under high pressure. This resulted in the heavier grades of oil yielding lighter oils and spirit. At

this time, however, there was not much call for light oils, and the process was not worked on a large scale.

As might be expected from his interest in oils for fuel and other purposes, he early took an interest in motor-cars, and more than twenty years ago the first four-cylinder Daimler car was constructed to his order and was exhibited to King Edward VII. (then Prince of Wales).

Besides his interest in his life-work, Redwood took very active interest in international exhibitions, and acted as chairman to the chemical section of the Royal Commissions for the Exhibitions of Brussels and Turin. He also served on the Committees of the Rome and St. Louis Exhibitions. He was a man of great activity and extreme conscientiousness, and beside looking after his business and advising his clients, served on committees of scientific societies, from which, when a member, he was rarely absent. It was, in fact, difficult to realise how he concentrated so much work within the working day.

During the war he served as Assistant Controller in the Trench Warfare Research. He was also Director of the Petroleum Research Department, and in this connexion supervised a large number of tests on the carbonisation of coals and other bituminous materials with the object of obtaining oils, so that this country might be self-contained and not require to procure the oils from abroad. Later he was appointed Director of Technical Investigations to the Petroleum Executive.

In 1913, at his instigation, the Institute of Petroleum Technologists was founded, and he was elected its first President.

Redwood was knighted in 1905 and received a baronetcy in 1911. The title passes to his grandson, Thomas Boverton Redwood.

Sir Boverton was adviser on petroleum to the Admiralty and Home Office, the India Office and the Colonial Office. He also acted as consulting adviser to the Corporation of London under the Petroleum Acts, and adviser to the Thames Conservancy. His treatise on petroleum, first published in 1896, is the standard English work on the subject. He wrote another work on petroleum in 1901 in conjunction with Captain J. H. Thomson, and published a number of papers on the subject before different industrial scientific societies.

As a man, Redwood had a most charming manner with an old-world courtesy. He was always willing to help the younger generation, and would take an infinite amount of trouble to help young men commencing their career. He was a staunch friend, and never spoke unkindly even of those with whom he did not agree. He had a habit when he met his friends of putting his

hands on their shoulders and saying, "Well, friend, and how are you to-day?" Those who knew Sir Boverton Redwood felt a very personal loss of a kind friend and counsellor. He died in harness, and only a few days before his death was enthusiastically examining the first oil struck in this country.

F. MOLLWO PERKIN.

JOHN CHARLES UMNEY.

BORN MARCH 13TH, 1868; DIED OCTOBER 9TH, 1919.

J. C. UMNEY was a pharmacist of a type that is none too common. He declared that he loved pharmacy, and was proud of being a pharmacist.

His father, Charles Umney, was a Fellow of the Chemical Society from 1865 until the time of his death in 1916, and an original Fellow of the Institute of Chemistry. He did pioneer work in bringing trained technical knowledge into the wholesale drug trade, and became one of the most prominent wholesale druggists of his day.

John Umney may thus be said to have been born into the drug trade. He was educated at Dulwich College, where he gained a scholarship, and at the Pharmaceutical Society's School of Pharmacy, where he was a medallist. After passing his examinations he worked in the Pharmaceutical Society's research laboratory under Professor Dunstan, with whom he was joint author of a paper on aconitine, which was published in the *Transactions* in 1892. He was elected a Fellow of the Society in the following year.

His first publication, made in 1889, was a note on the analytical characters of oil of anise. Thus did he early identify himself with essential oils, in connexion with which he is so well remembered. The literature of many essential oils has been enriched through his work, which consisted largely in the examination of new oils, of known oils from new sources, and occasionally of exposures of new and scientific methods of adulteration. Among others, he worked on the oils of anise, bergamot, cajuput, cloves, cinnamon, citronella, dill, eucalyptus, fennel, juniper, lavender, lemon, lemongrass, neroli, peppermint, pine, and rose, and his papers on the essential oils alone number upwards of fifty.

In 1912 the Fairchild Memorial Lectures delivered before the Pharmaceutical Society took the form of a short course of lectures on the terpenes and essential oils. The first of these, on "The History and Chemical Relations of the Terpenes," was delivered by Sir William Tilden; the second, on "The Synthesis of the Terpenes," by Professor W. H. Perkin. J. C. Umney was selected to give the third and fourth lectures, the title of which was "Essential Oils, their Constitution and Commerce."

Umney was a member of the Committee of Reference in Pharmacy concerned in the preparation of the 1914 edition of the British Pharmacopœia, and was part-author of the paper on "The Essential Oils of the British Pharmacopœia," which was read before the Pharmaceutical Society and formed the basis of the monographs now official in that book. He also contributed the article on "Essential Oils" in Thorpe's Dictionary of Applied Chemistry.

Umney published papers on fixed oils also, particularly almond, olive, cod liver, and fish liver oils, and many dealing with crude vegetable drugs, making valuable suggestions as to standards for these and other medicines.

His original contributions to pharmaceutical literature during a quarter of a century cover a wide range of subjects. In addition to scientific papers, and articles of a technical and commercial nature, he made valuable communications on subjects usually comprehended in the term "Pharmaceutical Politics." His publications were made chiefly in the *Pharmaceutical Journal*, and at the annual meetings of the British Pharmaceutical Conference. Latterly his communications appeared in *The Perfumery and Essential Oil Record*, which journal he himself founded and edited with conspicuous success.

At an unusually early age, in fact while still a student, John Umney began to exhibit signs of remarkable business capacity, and perhaps the most striking characteristic in his outstanding personality was his great executive ability.

Upon leaving the Pharmaceutical Society's research laboratory he entered his father's firm of wholesale druggists, and remained a director up to the time of his death. Sacrificing to some extent original work on the scientific side for the organising and more purely commercial aspects of pharmacy, John Umney rapidly reached a prominent position in the drug trade, and while still comparatively young was possibly the best known man in the world of pharmacy.

During the course of his business career he filled many offices, and in particular was President of the British Pharmaceutical Conference (1912–1913), President of the Drug Club (1908–1911),

and chairman of the Chemical Trade Section of the London Chamber of Commerce (1902–1916).

Prolific though he was as a contributor on pharmaceutical subjects, prominent and successful as he was as a business man, Umney was seen to greatest advantage in his public work, where his alert brain found full play. Possessed of keen and sound judgment, with a quick perception of the main issue to the exclusion of minor details, he was an invaluable man on the countless committees on which he was called to serve. A facile speaker, possessed of rare tact and great persuasive powers, Umney was at his best when acting as chairman of a meeting, a position he was called upon to fill on innumerable occasions.

Readily receptive of new ideas, innocent of obstinacy, possessing to a remarkable degree the gift of seeing the other man's point of view, Umney was an ideal colleague to work with, whether as joint-author, as fellow-councillor, or in commerce. As a business rival he was broadminded and generous. Indeed, those who knew him really well, and they have been many, will remember him most for his personal charm. Many since his death have testified to the valuable advice and kindly help which they have ungrudgingly received from him in cases of difficulty. Few pharmacists can have made so many strong personal friendships as John Umney.

The strain of his too-busy life weakened his constitution, and some five years ago ill-health, promoted by overwork, assailed him so seriously that he who had never spared himself willingly was now obliged to yield.

Notwithstanding his partial retirement from regular work, and despite the efforts of medical science, his health steadily grew worse, so that with accumulated infirmities he died at the comparatively early age of fifty-one. Thus did Pharmacy lose a leader, and many pharmacists a friend.

C. A. H.

Organic Chemistry.

Low Temperature Carbonisation. FRANZ FISCHER and W. GLUUD (*Ber.*, 1920, **53**, [*B*], 250—251).—The authors maintain their scientific and technical priority (compare A., 1919, i, 377) against Tern (this vol., i, 1). H. W.

The Interaction of Chlorine and Marsh Gas under the Influence of Light. The Conversion of Methyl Chloride into Methyl Alcohol and Methyl Acetate. JOHN REGINALD HARVEY WHISTON (T., 1920, **117**, 183—190).

Derivatives of Pentanes from Petroleum and certain of their Homologues. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1915, **58**, pp. 122; from *Chem. Zentr.*, 1918, ii, 939—941).—An account is given of the action of chlorine on the paraffins and of other substances prepared from the chloro-derivatives. The chief products investigated are the pentane mixture, b. p. 30—38°, a hexane, and a fraction, b. p. 10—12°, obtained during distillation of the pentanes. Starting from *iso*pentane, $CHMe_2Et$, it has been found possible to synthesise completely the main constituents of fusel oil, namely, the two primary *iso*amyl alcohols, *iso*butylcarbinol and *sec.*-butylcarbinol, which can thus be prepared cheaply and in unlimited quantity, since *iso*pentane occurs abundantly in all known mineral oils. The application of *iso*pentane and other suitable hydrocarbons from mineral oils (*n*-butane, *n*-pentane, and various hexanes, particularly βγ-dimethylbutane) to the preparation of isoprene and its homologues has been investigated. It is found that all the *iso*pentyl chlorides, certain of them therefore under isomerisation, lose hydrogen chloride under suitable conditions, with the formation of β-methyl-Δ^{β}-butylene; the latter unites with chlorine in definite circumstances to yield the corresponding dichloride, which is converted by the action of bases into isoprene. It is also found that the dichloro*iso*pentanes, obtained by direct chlorination of the hydrocarbon, and probably containing β-methyl-Δ^{β}-butylene chloride, lose hydrogen chloride at a sufficiently high temperature and yield isoprene.

I. *Derivatives of* iso*Pentane.*—Dry chlorination of *iso*pentane yields a mixture of the four *iso*pentyl chlorides, together with dichlorides, which are interesting on account of their relationship to isoprene. δ-*Chloro-β-methylbutane* has b. p. 99—102°, D_{15}^{15} 0·8692; α-*chloro-β-methylbutane*, b. p. 96—99°, D_{15}^{15} 0·8818; γ-*chloro-β-methylbutane*, b. p. 90—93°, D_{15}^{15} 0·8752; β-*chloro-β-methylbutane*, b. p. 85·5—88°, D_{15}^{15} 0·8692. β-*Methylbutyl acetate*, prepared from the corresponding *iso*amyl chloride, potassium acetate, and acetic acid at 190—200°, has b. p. 140—142°, D_{15}^{15} 0·8720, and, on hydrolysis, gives the corresponding *iso*amyl alcohol, b. p. 128·5—129·5°/

772 mm. *δ-Methylbutyl acetate* has b. p. 139—142°, and is converted by alcoholic potassium hydroxide into *γ-methylbutyl alcohol*, b. p. 130—133°. The constitution of the alcohols is decided by oxidising them to the corresponding valeric acids. β-Methyl-Δ^β-butylene (in addition to very little acetate) is the main product of the action of potassium acetate on *sec.-iso*amyl chloride and the sole product obtained from *tert.-iso*amyl chloride. For purposes of comparison, the latter was prepared by the action of hydrogen chloride on methylbutylene in anhydrous ether; it was found to be the sole product of the change, and to be entirely reconverted into methylbutylene by removal of hydrogen chloride. Attempts are described to obtain the *iso*pentyl acetates by the use of alcoholic potassium acetate, and it is found that the *iso*amyl chloride from fusel oil (containing much primary *iso*amyl chloride and little primary active *iso*amyl chloride, and therefore consisting of the most difficultly decomposed *iso*pentyl chlorides) is converted at 200° completely into amyl acetate and amyl alcohol. Moist chlorination of *iso*pentane leads to the production of small quantities of *sec.-iso*amyl chloride, large amounts of primary *iso*amyl chloride and primary active *iso*amyl chloride, and no *tert.-iso*amyl chloride. The best yields of monochloropentanes are obtained from light petroleum when it is subjected to dry chlorination, and it is found that *n*-pentane is less easily acted on than is *iso*pentane. The mixture of monochlorides obtained from *iso*pentane behaves towards alcohol and potassium acetate in the same manner as *iso*pentyl chloride from fusel oil. *iso*Pentyl chloride does not react with 2% potassium hydroxide solution at 60—70°. Only slight transformation occurs when *iso*amyl chloride is heated at 250°, more marked, but still incomplete, change at the same temperature in the presence of concentrated hydrochloric acid. Further chlorination of *tert.-iso*amyl chloride gives β-methyl-Δ^β-butylene chloride in unsatisfactory yield; the product which is thus obtained, as also the dichloride prepared by the direct chlorination of *iso*pentane, yields isoprene when heated with reagents which remove hydrogen chloride at 300—400°.

When the vapours of fermentation amyl alcohol are led over aluminium hydroxide impregnated with finely divided copper and heated at dull redness, β-methyl-Δ^β-butylene is mainly formed. Regulated chlorination of the latter gives mainly *iso*amylene chloride, $CH_2\dot{:}CMe{\cdot}CHMeCl$, and but little dichloride; probably a second chloroamylene, possibly $CMe_2Cl{\cdot}CH\dot{:}CH_2$, is also formed. The fraction, b. p. 90—100°, and the dichloride can be used in the preparation of isoprene. Different products are obtained when hydrogen bromide is removed from methylbutylene bromide by different bases. Elimination of both bromine atoms only occurs incompletely; β-bromo-γ-methyl-Δ^α-butylene is obtained in the pure condition by the use of alcoholic potassium hydroxide. Unsuccessful attempts are described to prepare the corresponding glycol by the oxidation of β-methyl-Δ^β-butylene with potassium permanganate.

The author describes experiments on the distillation of caoutchouc and on the conversion of isoprene obtained by heating the vapour of turpentine oil into its derivatives. The process first named yields only 1·9% of crude isoprene and 13% of a hydrocarbon (? terpene), b. p. 170—175°, which has not been more closely investigated. Pyrogenic decomposition of turpentine gives about 5% of crude isoprene, b. p. 30—40°; in the fraction b. p. up to 100°, at least two further hydrocarbons are found, one of which, b. p. ca 70°, occurs in particularly large amount and is unstable towards permanganate; the fractions of higher b. p. contain undecomposed terpenes, benzene, and its simpler homologues. The crude isoprene is purified by conversion into βδ-dibromo-β-methylbutane, b. p. 67°/9 mm., from which it is regenerated by potassium hydroxide; the pure isoprene has b. p. 34—34·5°/758 mm., D_{15}^{15} 0·6848, D_4^{20} 0·6811, n_D^{20} 1·41540. Experiments are also described on the conversion of technical crude isoprene into already known isoprene derivatives. It is found that not only amylene, but also all hydrocarbons which contain at least one true ethylenic linking, can be condensed with isoprene by means of aluminium chloride to yield similar condensation products. Conversely, hydrocarbons other than isoprene, which contain two conjugated double bonds, can be condensed with amylene and other singly unsaturated hydrocarbons. Variation of the relative amount of amylene and isoprene causes variation in the composition of the products. The author claims to have discovered the condensing action of sodium on isoprene independently of, and simultaneously with, Harries and Matthews; he obtained from crude isoprene and sodium a product, insoluble in alcohol but soluble in ether, which he terms "semicaoutchouc," which can be vulcanised. Sodium has no action on pure β-methyl-Δ^β-butylene. Pure isoprene, when heated alone during thirteen days, was less completely polymerised than after three days in the presence of sodium. Experiments on polymerisation by metallic oxides and on vulcanisation of semicaoutchouc are also described.

II. *Experiments with* n-*Pentane from Petroleum.*—A second *n-pentyl chloride*, b. p. 96—98°, is formed in addition to the previously described α-chloropentane, b. p. 106·6°, by the chlorination of *n*-pentane obtained from petroleum; an *iso*pentane derivative is not produced.

III. *Examination of Petroleum Fraction*, b. p. 10—12°.—When the fraction is chlorinated in the presence of water, the main product is a chloride, C_4H_7Cl, b. p. 69—70°, thus showing that it consists mainly of a butane; the presence of *iso*butane could be definitely established, but *n*-butane appears either to be absent or present in small quantity. The b. p. of *iso*butane has been given as −17°, but this can scarcely be correct. It is remarkable that, whilst the naturally occurring fatty acids have a normal carbon chain, the hydrocarbons obtained from petroleum have, in general, branched chains.

IV *Certain Hexane Derivatives from Petroleum.*—Preliminary

experiments on the chlorination of a hexane fraction, b. p. 58—60° and consisting chiefly of di*iso*propyl, led to the identification of both the possible monochloro-derivatives of this hydrocarbon, together with a third monochlorohexane, the constitution of which has not been elucidated. H. W.

Oxidation of Hydrocarbons by Oxygen. Oxidation of Paraffin. C. Kelber (*Ber.*, 1920, **53**, [*B*], 66—71).—Paraffin, vaselin, petroleums, and the higher fatty acids may be rapidly oxidised by submitting them to the action of finely divided streams of oxygen at 140—150°, especially in the presence of manganese compounds. In the case of a paraffin with m. p. 50—51°, 25% of the product was a distillate, consisting of oil and aqueous solution, in which acetone, formic, acetic, propionic, butyric, valeric, hexoic, octoic, nonoic, and decoic acids were identified. The pasty residue contained 40—50% of fatty acids insoluble in water, but soluble in light petroleum, and 5—10% of acids insoluble in petroleum.

J. C. W.

Nitration of Ethylene. Heinrich Wieland and Euklid Sakellarios (*Ber.*, 1920, **53**, [*B*], 201—210).—The hypothesis has been advanced by Thiele and elaborated by Holleman that substitution in the benzene series is preceded by addition, and that the primary reaction is similar in the ethylene and benzene series; in the former case the additive products, however, are stable, whilst in the latter, rearrangement immediately occurs, with the production of a more stable system. A certain amount of experimental evidence is available in the instances of halogenation and sulphonation, but very little work has been done on the nitration of ethylenic substances. The authors have therefore studied the behaviour of ethylene towards nitrating acid, and have shown that, under suitable conditions, ethylene dinitrate and nitroethyl nitrate are produced; it would thus appear that reaction is primarily additive in character, and results in the formation of β-nitroethyl alcohol, which, under the experimental conditions, is further esterified.

Ethylene is passed through an ice-cold mixture of nitric acid (D 1·4) and concentrated sulphuric acid containing 20% of sulphur trioxide, and the products are separated by distillation with steam and subsequent careful fractionation under diminished pressure; ethylene dinitrate, colourless oil, b. p. 105·5°/19 mm., D^{17} 1·433, and *β-nitroethyl nitrate*, colourless, poisonous oil, b. p. 120—122°/17 mm., D^{18} 1·468, are thus isolated. The latter is converted by phosphoric oxide into nitroethylene (compare A., 1919, i, 307).

Discrepancies between the properties of specimens of β-nitroethyl alcohol obtained by the authors and those described by V. Meyer and Henry have led them to examine in greater detail the action of silver nitrite on ethylene iodohydrin; it is found that the substance which is thus prepared is contaminated with ethylene glycol mononitrite, which can be removed by careful fractionation, and

with ethylene glycol, which cannot be thus removed, but is readily eliminated by washing the product with water. Pure β-nitroethyl alcohol is a colourless, odourless liquid, b. p. 103°/11·5 mm., $D^{15.3}$ 1·309; it is miscible in all proportions with water, alcohol, and ether. The aqueous solution does not give a coloration with ferric chloride, and the ketonic form can only be detected for a few seconds with this reagent after cautious acidification of the sodium salt. Contrary to Henry's observations, it cannot be distilled at the ordinary pressure, since it is thereby decomposed into water and nitroethylene.

Attempts to isolate nitroacetaldehyde in substance have not been successful up to the present; if, however, a mixture of β-nitroethyl alcohol and sulphuric acid is added to a boiling suspension of lead peroxide in water and the distillate is treated with o-nitrophenylhydrazine hydrochloride, *nitroacetaldehyde-o-nitrophenylhydrazone*, slender, orange-red needles, m. p. 83·5°, is obtained.

H. W.

Preparation of Propylene. ARTHUR HEINEMANN (D.R.-P. 315747; from *Chem. Zentr.*, 1920, ii, 186).—Acetylene is caused to unite with methane in the presence of contact substances consisting of mixtures of noble metals (platinum, iridium, and palladium) and common metals (iron, nickel, copper, silver, aluminium). The technical preparation of the contact agent is effected by depositing the common metal, such as copper, either electrolytically or by purely chemical reduction of a copper salt on a porous material, such as pumice; the latter is placed in a solution of a noble metal (for example, platinous chloride), dried, and, if necessary, again reduced. Methane is completely utilised at 100—200° if an excess of acetylene is employed. The heating may be replaced by the chemically active violet or ultra-violet rays, or by the silent electric discharge. The yield of propylene is 70% of that theoretically possible.

H. W.

The Action of Nitric Acid on Unsaturated Hydrocarbons. The Action of Nitric Acid on Acetylene. KENNEDY JOSEPH PREVITÉ ORTON and (MISS) PHYLLIS VIOLET MCKIE (T., 1920, 117, 283—296).

Preparation of Methyl Chloride and Bromide from Methyl Sulphate. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 595—597).—Methyl chloride may readily be prepared in a very pure state and with an excellent yield by allowing methyl sulphate to drop into hydrochloric acid (D 1·112) at about 50°, the change occurring being represented by $Me_2SO_4 + HCl = MeHSO_4 + MeCl$. The hydrochloric acid may be replaced by a concentrated solution of sodium chloride, but in this case a slightly higher temperature is necessary.

In the same way, methyl bromide may be obtained by letting

methyl sulphate drop into hydrobromic acid at 45—50°, or, preferably, into a concentrated solution of an alkali bromide, slightly acidified with sulphuric acid, at 30—35°. W. G.

Organic Chemical Reagents. V. The Preparation of Alkyl and Alkylene Bromides. OLIVER KAMM and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1920, **42**, 299—309).—A detailed study has been made of the preparation of *n*-butyl bromide from the corresponding alcohol by the hydrobromic acid method; addition of sulphuric acid to the reaction mixture was found to be of more value than an increase in the quantity of hydrobromic acid. The effectiveness of sulphuric acid does not depend entirely on the resulting removal of water from the reaction mixture, but is also to be explained by the formation of an alkyl hydrogen sulphate, which probably reacts more readily with hydrobromic acid; the effect of sulphuric acid in preventing the distillation of alcohol from the reaction mixture is also an important factor.

The Norris-Bodroux method for the preparation of primary alkyl bromides has been modified in the following manner. The alcohol is treated with a 25% excess of aqueous hydrobromic acid, together with sulphuric acid. The mixture is heated under reflux in order to convert the alcohol as completely as possible into the corresponding bromide, and the latter is then removed from the reaction mixture by direct distillation. Slight variations from this procedure depend on the physical and chemical properties of the alcohol used or of the bromide formed in the reaction. For example, in the preparation of ethyl and allyl bromides, the mixture is not heated under reflux, because of the volatility of the former compound and the chemical reactivity of the latter; in the preparation of *iso*amyl bromide, a somewhat smaller proportion of sulphuric acid is used in order to prevent charring; haloids of high molecular weight, because of their high boiling points, are separated from the reaction mixture mechanically instead of by distillation. Detailed directions are given for the preparation of the following compounds, the corresponding yields being enclosed within brackets: *n*-butyl bromide, b. p. 101—104° (95—97%); *iso*amyl bromide, b. p. 116—120° (88—90%); trimethylene bromide, b. p. 162—165° (88—95%); trimethylene chlorobromide, b. p. 142—145° (89%); ethyl bromide, b. p. 38—40° (90—95%); allyl bromide, b. p. 69—72° (92—96%); *n*-octyl bromide, b. p. 196—200° (91%); lauryl bromide, b. p. 175—180°/45 mm. (91%).

The requisite hydrobromic acid solution is conveniently prepared by the reduction of bromine by sulphur dioxide in the presence of water; the mixture may be utilised directly without a preliminary distillation, the necessary additional quantity of sulphuric acid being added as concentrated acid.

Mixtures of constant boiling hydrochloric and hydrobromic acids, such as are obtained when alkyl bromides are used with aluminium chloride in Friedel-Crafts' reactions, may be separated readily by fractional distillation. H. W.

Gaseous Methyl Fluoride. I. Revision of the Atomic Weight of Fluorine. E. MOLES and T. BATUECAS (*J. Chim. Phys.*, 1919, **17**, 537—588).—The methyl fluoride was prepared either by heating together methyl potassium sulphate and potassium fluoride or by passing the vapour of methyl iodide over anhydrous silver fluoride at 90°. The weight of a normal litre of methyl fluoride was found to be 1·5454 grams, whilst measurements made at 506·67 mm. and 253·33 mm. indicate that the departure from Avogadro's law is given by $1+\lambda=1\cdot0181$, and the coefficient of compressibility of methyl fluoride is 0·000037 per mm. The weight of a normal litre of oxygen under similar conditions was 1·4293, hence the molecular weight of methyl fluoride is 34·021 and the atomic weight of fluorine is 18·998.

Measurements of the vapour pressure of methyl fluoride between −77° and −105° give as its b. p. −78·2°/760 mm. The molecular heat of vaporisation, calculated by the Clausius-Clapeyron formula, is $\lambda=4361$ cal., and from this the Ramsay-Trouton constant is found to be 22·4. The critical temperature deduced by the Guldberg-Guye rule is $T_c=325\cdot3°$.

In the preparation of methyl fluoride by the action of methyl iodide on silver fluoride, a brick-red compound is formed, which has the composition 2AgF,AgI. W. G.

The Dehydrogenation of Primary and Secondary Alcohols by Catalytic Oxidation. General Method of Preparation of Aldehydes and Ketones. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, **170**, 258—261).—Finely divided silver, deposited on asbestos by precipitation from silver nitrate with formaldehyde, is an excellent catalyst for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively. The vapour of the alcohol, mixed with slightly less than the theoretical amount of air, is passed over the catalyst heated at 230—300°. In some cases the action is so intense as to cause very marked local rise in temperature of the catalyst, and consequent destruction of some of the products of oxidation. In this case, it is better to conduct the operation in two stages. First pass the alcohol vapour, mixed with 40—50% of the requisite amount of air, over the catalyst, and then mix the issuing vapours with the other 50% of air and pass the new mixture over a second lot of the catalyst. Good results were obtained with methyl, ethyl, butyl, amyl, allyl, benzyl, cinnamyl, *iso*propyl, and secondary butyl alcohols by this method. W. G.

Organic Chemical Reagents. VI. Reagents from *n*-Butyl Alcohol. ROGER ADAMS and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1920, **42**, 310—320).—The discovery of the method by which starch may be fermented to give acetone and *n*-butyl alcohol has caused the latter substance to become available in large quantity at a low price. The authors show it to be a valuable material for the preparation of *n*-amyl derivatives and *n*-hexoic

acid and its derivatives. Detailed instructions are given for the preparation of the following substances, the yields being placed within brackets: *n*-butyl bromide (this vol., i, 282); *n*-butyl cyanide, b. p. 138—141°, from the bromide and sodium cyanide in aqueous-alcoholic solution (75—80%); *n*-valeric acid, b. p. 183—186°, from butyl bromide and sodium cyanide, and hydrolysis of the crude product with sodium hydroxide (81%); ethyl *n*-valerate, b. p. 142—146°, from *n*-butyl cyanide, ethyl alcohol, and sulphuric acid (85—90%); *n*-amylamine, b. p. 102—105°, by addition of a solution of *n*-butyl cyanide in alcohol to a suspension of sodium in toluene (57—68%); *n*-amyl alcohol, by reduction of ethyl *n*-valerate by sodium in the presence of alcohol (56—61%); ethyl *n*-butylmalonate, b. p. 144—145°/40 mm., 235—240°/ordinary pressure, from *n*-butyl bromide and ethyl sodiomalonate (89—92%); *n*-hexoic acid, b. p. 200—205°, by hydrolysis of ethyl *n*-butylmalonate with potassium hydroxide, acidification of the solution with hydrochloric acid, and subsequent distillation (74%); α-bromohexoic acid, b. p. 148—153°/30 mm., by bromination of *n*-butylmalonic acid and elimination of carbon dioxide from the product (71%); α-aminohexoic acid, from the α-bromo-acid and ammonia (65%). H. W.

Synthesis of Tertiary α-Keto-alcohols: Correction. D. GAUTHIER (*Compt. rend.*, 1920, **170**, 325).—It has previously been indicated that cyanohydrins of the type $HO\cdot CR^1R^2\cdot CN$ react with organo-magnesium haloids, R^3MgX, to give α-ketonic tertiary alcohols, $HO\cdot CR^1R^2\cdot COR^3$ (compare A., 1911, i, 513). It has since been found that the main product of such a reaction is the tertiary alcohol, $CR^1R^2R^3\cdot OH$. Consequently, the substance previously described as acetyldimethylcarbinol, $CH_3\cdot CO\cdot CMe_2\cdot OH$, is really trimethylcarbinol, and the two substances described as propionyldimethylcarbinol, $C_2H_5\cdot CO\cdot CMe_2\cdot OH$, and acetylmethylethylcarbinol, $CH_3\cdot CO\cdot CMeEt\cdot OH$, are really dimethylethylcarbinol. W. G.

Catalytic Preparation of Ethers in the Dry Way. A. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], 27, 121—126; *Compt. rend.*, 1920, **170**, 329—331).—Using the method previously described for the catalytic preparation of ethyl ether (this vol., i, 6), calcined alum being the catalyst, the authors have succeeded in preparing a number of simple and mixed aliphatic ethers from the corresponding alcohols up to *iso*amyl alcohol. *iso*Propyl alcohol and *iso*butyl alcohol only gave very small yields of the corresponding ethers. W. G.

Action of Water on Methyl Chlorosulphonate. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, **170**, 326—328).—The action of water on methyl chlorosulphonate depends on the relative

amounts of water and sulphonate present. The action is complex and is regulated by three changes, thus:

$$SO_2Cl\cdot OMe + 2H_2O = H_2SO_4 + HCl + MeOH,$$
$$SO_2Cl\cdot OMe + H_2O = H_2SO_4 + MeCl,$$
$$SO_2Cl\cdot OMe + H_2O = HMeSO_4 + HCl,$$

with which, under some conditions, are joined the actions:

$$HCl + MeOH = MeCl + H_2O,$$
$$HMeSO_4 + MeOH = H_2SO_4 + Me_2O.$$

The primary change is the one which produces methyl hydrogen sulphate, which is, in its turn, decomposed by an excess of water to give sulphuric acid and methyl alcohol. The latter change is limited by the reverse action, but for a large excess of water the proportion of methyl hydrogen sulphate remaining is small and independent of the amount of water.

When the amount of water diminishes, the concentration of the acids becomes important, the esterification of the methyl alcohol becomes of main importance, and consequently a more and more marked synthetic production of methyl chloride occurs. W. G.

Action of Water on Methyl Sulphate. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, **170**, 392—394).—If a large excess of water acts on methyl sulphate for a relatively short time, a unimolecular reaction occurs, thus: $Me_2SO_4 + H_2O = MeHSO_4 + MeOH$.

If the proportion of sulphate to water is 1:10, at the end of twenty-four hours a second action is noticeable, $Me_2SO_4 + H_2O = H_2SO_4 + Me_2O$, and this action becomes preponderant. At the same time, a secondary change may occur, $Me_2SO_4 + MeOH = MeHSO_4 + Me_2O$.

Methyl sulphate is, however, soluble in water at 18° to the extent of 28 grams per litre, this solubility being modified by the accumulation of the sulphuric acid and methyl ether resulting from the above changes. W. G.

The Sulphochromic Combustion of Methyl Esters. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, **170**, 514—516).—The esters were oxidised by chromic anhydride in the presence of sulphuric acid, the carbon dioxide liberated being collected in a Bunte burette and measured. In some cases, the reacting mixture required heating in a water-bath. Satisfactory results were obtained with all the esters tried. The change apparently takes place in two stages, methyl hydrogen sulphate being first formed, $R\cdot CO_2Me + H_2SO_4 \rightleftharpoons R\cdot CO_2H + MeHSO_4$, and oxidation then occurring.

Under similar conditions, ethyl esters undergo little or no oxidation, except in those cases where the organic acid radicle is readily oxidised, in which case ethyl hydrogen sulphate is formed and the organic acid is oxidised.

Substituted radicles, whether methyl or ethyl, do not undergo oxidation at all readily. Thus, methyl malonate is readily oxidised, but with methyl methylmalonate the oxidation is very incomplete.

W. G.

ββ′-Dichloroethyl Sulphide. CHARLES STANLEY GIBSON and (SIR) WILLIAM JACKSON POPE (T., 1920, **117**, 271—278).

A Synthesis of ββ′-Dichlorodiethyl Sulphide (Mustard Gas). J. E. MYERS and H. STEPHEN (*J. Soc. Chem. Ind.*, 1920, **39**, 65T).—By passing pure ethylene into cooled sulphur dichloride until no further absorption takes place, a product containing 65% of mustard gas with 20—25% of sulphur monochloride is obtained. The formation of the latter compound, together with the evolution of considerable quantities of hydrogen chloride, is probably due to the decomposition of sulphur dichloride into the monochloride and chlorine, which then chlorinates the mustard gas. This secondary reaction is best avoided by spraying the dichloride (a mixture of 75% dichloride and 25% monochloride being most suitable) by means of compressed ethylene into an atmosphere of ethylene. In this manner, a product containing 93% mustard gas is obtained.

A solution of sodium hypochlorite containing sodium hydrogen carbonate was found to remove mustard gas almost immediately from the surface of shells. J. K.

ββ′-Dichloroethyl Sulphide. P. SPICA (*Gazzetta*, 1919, **49**, ii, 299—302; *Boll. chim. farm.*, 1919, **58**, 361—363).—The author has prepared ββ′-dichloroethyl sulphide by a method which is not described, but is simpler than that originally used by V. Meyer. This compound forms long, silky, white needles, m. p. 10—11°, b. p. 180—185°/20—25 cm., 215—217° (decomp.); in the liquid state it has D^{15} 1·275, and is colourless, its odour recalling that of garlic. It is an oxidisable compound, and on this property depends the use of calcium hypochlorite, potassium permanganate, etc., to neutralise its effects. Concentrated nitric acid acts slowly on it and yields varying results, but the action of 30% hydrogen peroxide solution in glacial acetic acid gives first the sulphoxide,

$$(CH_2Cl{\cdot}CH_2)_2SO,$$

m. p. 50—52°, which acts as an irritant on the eyes and skin, especially when vaporised from solution, and afterwards the sulphone, $(CH_2Cl{\cdot}CH_2)_2SO_2$, m. p. 110°, which is almost non-volatile in a current of steam and exerts no irritating action.

Of the various reagents proposed for the detection of ββ′-dichloroethyl sulphide, the only one which is specific is sodium iodide, this giving the corresponding di-iodo-compound. The presence of vapour of the sulphide in the air may also be detected by the formation of the sulphone occurring when the air is passed through a glacial acetic acid solution of hydrogen peroxide (see above), and also by the white turbidity, due to the formation of Meyer's non-

resolvable diethylene disulphide, produced when the air is passed through a narrow tube into hot sodium sulphide solution.

T. H. P.

Synthetical Experiments with ββ′-Dichloroethyl Sulphide. WILLIAM DAVIES (T., 1920, **117**, 297—308).

***iso*Amylsulphonium Compounds.** RUDOLF WEGSCHEIDER and HELENE SCHREINER (*Monatsh.*, 1919, **40**, 325—339).—Only a slight quantity of sulphonium compound was produced by the interaction of *iso*amyl iodide with di*iso*amyl sulphide for five months. This was not due to steric influences, since, although the velocities of combination of the sulphide with methyl, ethyl, and *iso*amyl iodides diminish in the order given, that of the sulphide with ethyl iodide is much greater than in the case of ethyl sulphide and *iso*amyl iodide. As the equation, $SR^1R^2 + R^3I = SR^1R^2R^3I$, shows, the speed of the reaction is primarily determined by the mobility of the halogen atom (compare Carrara, A., 1895, ii, 8; Strömholm, A., 1900, i, 325). In conformity with this explanation, *iso*amyl iodide cannot be prepared from the corresponding chloride in the same manner as can benzyl iodide (Späth, A., 1914, i, 1). Double salts of tri*iso*amylsulphonium iodide with zinc, cadmium, and mercuric iodides can, however, easily be prepared by warming mixtures of *iso*amyl iodide and sulphide with the metallic iodide at 100°. *Bistri*iso*amylsulphine zinci-iodide*, $2S(C_5H_{11})_3I,ZnI_2$, has m. p. 134°; the corresponding *cadmi-iodide*, $2S(C_5H_{11})_3I,CdI_2$, forms yellow needles, m. p. 126—127°, and is decomposed by hot water; the dimercuri-iodide, $3S(C_5H_{11})_3I,2HgI_2$, forms light yellow crystals, m. p. 66—67° to a turbid liquid, becoming clear at a somewhat higher temperature. An indefinite product was obtained from bismuth iodide. Tri*iso*amylsulphonium iodide could not be liberated from its salts, but was probably produced by prolonged action of the iodide on the sulphide in presence of molecular silver. *Diethyl sulphide dimercurichloride*,

$$S(C_2H_5)_2,2HgCl_2,$$

separates from alcohol in colourless crystals, m. p. 127°, which are decomposed by water.

J. K.

Preparation of Acetic Anhydride. FREDERICK PEACOCK LEACH and THE UNITED ALKALI CO., LTD. (Brit. Pat. 137701).—Acetic anhydride is produced by the interaction of anhydrous sodium acetate and carbonyl chloride according to the equation $2CH_3{\cdot}CO_2Na + COCl_2 = (CH_3{\cdot}CO)_2O + CO_2 + 2NaCl$. The reaction is started by suspending sodium acetate in acetic anhydride and adding alternately, with cooling, carbonyl chloride and sodium acetate, keeping the latter in slight excess, until a desired amount of the mixture has been produced. A portion of the liquor is then run off into a still, and the acetic anhydride distilled off in a vacuum, whilst fresh quantities of sodium acetate and carbonyl chloride are added to the mixture remaining in the reaction vessel.

G. F. M.

Preparation of Aliphatic Acids by Catalytic Oxidation of Primary Alcohols. A. MAILHE and F. DE GODON (*Compt. rend.*, 1920, **170**, 517—519).—Primary aliphatic alcohols readily undergo catalytic oxidation in the presence of finely divided copper at 260—270°, giving an appreciable yield of the corresponding acids, but at the same time an important amount of the aldehyde is also formed. In the case of ethyl alcohol, the highest yield obtained was 18·18 grams of acetic acid and 12 c.c. of acetaldehyde from 100 c.c. of alcohol. W. G.

Preparation of Aliphatic Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 315021; from *Chem. Zentr.*, 1919, iv, 1104).—Acetylene is allowed to act on a molar mixture of fatty acid and alcohol in the presence of the mercury salts of mineral acids, preferably at an increased temperature. Thus, acetic acid is agitated with precipitated mercury oxide at 30—40° until complete solution is obtained, after which sulphuric acid (D 1·81) is added drop by drop, which causes the precipitation of mercuric sulphate in a finely divided condition; after addition of ethyl alcohol, the mixture is heated at 70° under reflux, and, with constant agitation, treated with acetylene. Acetaldehyde, which is formed as a by-product, is separated from ethyl acetate by fractional distillation. Ethyl formate is obtained when the acetic acid is replaced by formic acid, whilst methyl propionate is prepared from methyl alcohol and propionic acid. H. W.

Preparation of α-Sulphopropionic Acid. H. J. BACKER and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 415—416).—The general methods of Franchimont (A., 1888, 1175) and of Melsens, when applied to the preparation of α-sulphopropionic acid, have the respective advantages of greater purity and better yield of the product. Both of these are conserved by a combination of the two processes, consisting in the addition of crystalline pyrosulphuric acid to propionic anhydride. An average yield of 0·75 mol. of acid per 1 mol. of anhydride is thus obtained. J. K.

Ammonium Tetroxalate, a Product of the Decomposition of *iso*Amyl Nitrite. H. SANDQVIST and E. MOHLIN (*Ber.*, 1920, **53**, [*B*], 171—173).—A crystalline deposit, needles or rods, m. p. 129·5—130·5° (decomp.), deposited on the sides of a bottle containing commercial amyl nitrite which had become extensively decomposed, was found to consist of ammonium tetroxalate. Formation of these crystals in similar circumstances has been observed by Bödtger (A., 1916, i, 2), who, however, overlooked the nitrogen content, and considered them to be methanetetracarboxylic acid. H. W.

***l*-Hexylsuccinic Acid.** HENRY WREN and HENRY BURNS (T., 1920, **117**, 266—268).

The Resolution of Racemic Acids by Optically Active Alcohols. I. The Resolution of *r*-Tartaric Acid by *l*-Borneol. HENRY WREN, HOWELL WILLIAMS, and WILLIAM WHALLEY MYDDLETON (T., 1920, **117**, 191—199).

Preparation of Succinyldiacetic Esters. RICHARD WILLSTÄTTER (D.R.-P. 300672; from *Chem. Zentr.*, 1920, ii, 338).—Neutral or faintly acid solutions of acetonedicarboxylic acid esters are submitted to electrolysis. The secondary potassium salts of acetonedicarboxylic acid ester are obtained by the action of potassium hydroxide in concentrated aqueous or in alcoholic solution on acetonedicarboxylic esters. The dipotassium salt of ethyl hydrogen acetonedicarboxylate yields, on electrolysis, *ethyl succinyldiacetate*, colourless needles, m. p. 46—47°, which with ammonia or amines yields pyrrole derivatives, for example, 1-*methylpyrrolediacetic ester*, prisms, m. p. 164°. The corresponding methyl derivative of succinyldiacetic acid is formed less smoothly from methyl hydrogen acetonedicarboxylate, and is converted into *dimethyl* 1-*methylpyrrolediacetate*, needles, m. p. 170—171°. The succinyldiacetic ester constitutes the starting point for the synthetic preparation of derivatives of tropine. H. W.

The Preparation of Glyoxal by the Action of Ozone on Acetylene. A. WOHL and K. BRÄUNIG (*Chem. Zeit.*, 1920, **44**, 157).—It is well known that ozone and acetylene interact with explosive violence. It has now been found that when the gases are suitably diluted and contain a certain amount of moisture, interaction proceeds smoothly, with formation of a mixture of glyoxal and formic acid. The products are obtained as an aqueous solution by spraying water into the reaction vessel. The solution contains 1·5 to 2·0% of glyoxal. A certain amount of nitric acid is formed at the same time, and this must be neutralised before the solution is evaporated, to avoid decomposition of the glyoxal. The latter can be isolated by known methods, for example, as its aniline derivative, or can be directly converted into glycollic acid or ethylene glycol. The aniline derivative, the anilide of anilinoacetic acid, can be used for the preparation of indigotin. E. H. R.

Preparation of Monobromoacetone. J. D. RIEDEL (D.R.-P. 298944; from *Chem. Zentr.*, 1920, ii, 337).—Solutions of bromine in bromide liquors are added to hot solutions of acetone containing bromoacetone in bromide liquors; the latter are obtained by neutralising the aqueous solutions from previous preparations. Monobromoacetone is thus obtained in good yield and in an immediately pure condition. H. W.

Preparation of Monobromo-ketones. J. D. RIEDEL (D.R.-P. 298953, additional to D.R.-P. 298944; from *Chem. Zentr.*, 1920, ii, 337. Compare preceding abstract).—Solutions of bromine in bromide liquors are added at an elevated temperature to solutions of the homologues of acetone (containing the bromo-ketone) or to a mixture of ketones and bromide liquors; the neutralised aqueous solutions from previous preparations are utilised as bromide liquors.

The instance of bromomethyl ethyl ketone, transparent, yellow liquid, is cited in particular. H. W.

A New Hydrazone of some Monosaccharides (*m*-Tolylhydrazones of *l*-Arabinose, Rhamnose, Fucose, *d*-Galactose, and *d*-Mannose). A. W. van der Haar (*Rec. trav. chim.*, 1920, **39**, 191—193).—*m*-Tolylhydrazine gives the following hydrazones: l-*arabinose*-m-*tolylhydrazone*, prismatic needles, m. p. 156—157°; *rhamnose*-m-*tolylhydrazone*, m. p. 134°; *fucose*-m-*tolylhydrazone*, microscopic needles, m. p. 165°; d-*mannose*-m-*tolylhydrazone*, amorphous; d-*galactose*-m-*tolylhydrazone*, needles, m. p. 154°. Xylose and *d*-fructose did not give such hydrazones, and the one from dextrose could not be obtained sufficiently pure. W. G.

Oxidation of Sugars by Mercuric Acetate in the Presence of Ammonia. T. Ingvaldsen and L. Bauman (*J. Biol. Chem.*, 1920, **41**, 147—148).—Ammonium gluconate and ammonium galactonate may be obtained in 50% yield by the action of mercuric acetate on dextrose or galactose in the presence of ammonia. Mannose and lactose are also oxidised by this method, but the ammonium salts of the acids formed have not been isolated in crystalline form. J. C. D.

The Heptoses from Gulose and some of their Derivatives. F. B. La Forge (*J. Biol. Chem.*, 1920, **41**, 251—256).—Gulose was converted into a mixture of α- and β-guloheptonic acids by the cyanide synthesis. A mixture of the barium salts yielded on crystallisation rosettes of plates of the barium salt of α-guloheptonic acid, $C_{14}H_{26}O_{16}Ba$.

α-*d*-Guloheptonic acid was a colourless syrup, which did not crystallise. It yielded a crystalline *phenylhydrazide*, long, white needles, m. p. 191—192° (uncorr.), $[\alpha]_D^{20}$ −15·38°.

α-d-*Guloheptose*, $C_7H_{14}O_7$, obtained by reduction with sodium amalgam, forms rosettes of long needles, m. p. 185—187° (uncorr.), $[\alpha]_D^{20}$ −65·65°.

α-Guloheptitol, $C_7H_{16}O_7$, rosettes of hard prisms, m. p. 138—141° (uncorr.). No rotation was shown by an approximately 5% solution in water. 1·0624 Grams in 25 c.c. of saturated borax solution gave in a 4-dcm. tube α_D +0·68°.

β-Guloheptonic acid and β-*guloheptose* were obtained from the mother liquors of the barium salt of α-guloheptonic acid. On reduction of the syrupy β-guloheptose, another syrup was obtained, which, as it did not crystallise, was converted into *benzylidene-β-guloheptitol*, m. p. 260° (decomp.).

β-*Guloheptitol*, $C_7H_{16}O_7$, has m. p. 128—129° (uncorr.). 0·3175 Gram in 5 c.c. of saturated borax solution showed no appreciable rotation in a 1-dcm. tube. J. C. D.

The Constitution of the Disaccharides. IV. The Structure of the Fructose Residue in Sucrose. Walter Norman Haworth (T., 1920, **117**, 199—208).

Biochemical Synthesis of a Mannobiose. EM. BOURQUELOT and H. HERISSEY (*J. Pharm. Chim.*, 1920, [vii], **21**, 81—85).—The enzyme seminase (A., 1900, i, 320) obtained from lucerne seeds, when kept for ten months in concentrated mannose solution containing a small quantity of toluene, converted the mannose, in part, into a sugar having a higher optical rotation. This sugar was isolated in an impure state, and appeared to be a mannobiose.
W. P. S.

Determination of the Value of Different Acids for the Liquefaction of Starch. P. BETTINGER (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 126—131).—The relative activities of hydrochloric, sulphuric, and certain organic acids in producing liquefaction of the starch in ground cereals, under similar conditions of heating, are accounted for by the different degrees of ionisation of the acids. [See, further, *J. Soc. Chem. Ind.*, 1920, 244A.] J. H. L.

Action of Saliva Ash on Starch Solution. FR. N. SCHULZ (*Fermentforsch.*, 1919, **3**, 72—74; from *Chem. Zentr.*, 1920, i, 8—9).—In repeating Biedermann's experiments (this vol., i, 15) with saliva ash, the author has encountered the same difficulties as Wohlgemuth and Sallinger. Since the ash was strongly alkaline in reaction, whilst Biedermann describes the use of a neutral or faintly acid ash, and, on the other hand, the dependence of diastatic processes on the reaction is well known, the ash was made very faintly acid with hydrochloric acid. Reaction was immediately observed, which could be stopped by addition of an excess of the acid. The time of action varied between twenty minutes and several (generally four to six) hours. Optimum action probably depends on the absolute quantity of ash and a definite degree of acidity. Urine ash, when kept faintly acidic, invariably gives a positive result. H. W.

Autolysis of Starch. Reply to Wohlgemuth and Sallinger. W. BIEDERMANN (*Fermentforsch.*, 1919, **3**, 70—71; from *Chem. Zentr.*, 1920, i, 9. Compare this vol., i, 15).—The discordant results obtained by Wohlgemuth (A., 1919, i, 361) and Sallinger (this vol., i, 15) are explained by the different reaction of the saliva ash in the various instances. The ash used by the author was neutral or very faintly acidic; it now appears that this behaviour is exceptional, and that the hydrolysis of starch by saliva ash is dependent on the reaction of the latter, as is to be expected from the known influence of alkali on amylase action (compare Schulz, preceding abstract). H. W.

Lignin. II. Fusion of the Lignosulphonic Acids with Potassium Hydroxide. MAX HÖNIG and WALTER FUCHS (*Monatsh.*, 1919, **40**, 341—349).—The removal of the sulphonic groups from the barium salts previously described (A., 1918, i, 375) by fusion with potassium hydroxide is only complete at 250—300°. In each case, protocatechuic acid is the sole product (compare Melander,

A., 1919, i, 473) obtained after solution of the fused mass in water, acidification, filtration from insoluble matter (amounting to about one-third of the purely organic portion of the original material), and extraction with ether, the quantity obtained corresponding with 13—19% of the organic portion of the original material. In addition, a small quantity of material is not removed from the aqueous solution by ether. The lignosulphonic acids are therefore complicated aromatic sulphonic acids containing the carbon skeleton of protocatechuic acid. J. K.

Preparation of Methylamine from Ammonium Methyl Sulphate. WILLIAM SMITH DENHAM and LIONEL FREDERICK KNAPP (T., 1920, **117**, 236—247).

Double Salts of Cerium Tetrachloride. F. DI STEFANO (*Annali Chim. Appl.*, 1919, **12**, 130—136).—Owing to the instability of quadrivalent cerium, the tetrachloride of that metal has not been isolated, but Koppel (A., 1899, ii, 98) prepared stable double salts of cerium tetrachloride with pyridine, quinoline, and triethylamine, which he concluded to be derivatives of a hydrochloroceric acid, H_2CeCl_6. Various new double salts of this acid are now described. The *tetramethylammonium* salt,

$$CeCl_4,2N(CH_3)_4Cl,$$

was prepared by adding a concentrated solution of tetramethylammonium chloride in methyl alcohol to a solution of ceric chloride in the same solvent, and washing the resulting yellow, crystalline precipitate first with methyl alcohol saturated with hydrogen chloride, and then with ether. It is stable in absolutely dry air, but completely decomposed on exposure to moist air, and when dissolved in water rapidly liberates chlorine. The *tetraethylammonium* salt, $CeCl_4,2N(C_2H_5)_4Cl$, is obtained in an analogous manner. It is much more stable than the preceding compound, and is only slowly decomposed when dissolved in water. It liberates iodine from potassium iodide (ratio of Ce to active Cl = 1:0·99). The *caffeine* salt, $CeCl_4(C_8H_{10}O_2N_4,HCl)_2$, forms reddish-orange, silky crystals which are quite stable in dry air, and only decompose slowly in moist air (ratio of Ce to active Cl = 1:1·06). Theobromine hydrochloride gave a yellow, crystalline powder with cerium tetrachloride, the exact composition of which could not be determined owing to the presence of the excess of alkaloid hydrochloride, but was probably $CeCl_4,2(C_7H_8O_2N_4,HCl)$. The *quinine* salt, $CeCl_4,2(C_{20}H_{24}O_2N_2,2HCl)$, was obtained in large, reddish-orange crystals, in which the ratio of cerium to active chlorine was 1:1. C. A. M.

A New Method for the Preparation of Hexamethylenetetramine. WALTHER HERZOG (*Zeitsch. angew. Chem.*, 1920, **33**, 48).—If commercial ammonium carbonate is treated with 40% formaldehyde solution, it readily dissolves, even without application of heat, with brisk evolution of carbon dioxide and formation of hexamethylenetetramine. The solution is evaporated to dryness on a

water-bath under reduced pressure, and the residue is either sublimed in a vacuum or recrystallised from absolute alcohol. The amount of ammonium carbonate should be about 10% in excess of the theoretical quantity. A yield of about 66% is obtained.

W. J. W.

Solubility of Hexamethylenetetramine. F. UTZ (*Süddeutsch. Apoth. Zeit.*, 1919, **59**, 832; from *Chem. Zentr.*, 1920, i, 170).—1·67 Grams of hexamethylenetetramine dissolve in one part of water at the ordinary temperature (D 1·0985); larger quantities dissolve in hot water and separate on cooling the solution. At the ordinary temperature, 100 c.c. of the solvents dissolve the following amounts of hexamethylenetetramine, expressed in grams: ethyl ether, 0·06 (on warming, 0·38); trichloroethylene, 0·11; xylene, 0·14; carbon disulphide, 0·17; benzene, 0·23; tetrachloroethane, 0·50; acetone, 0·65; carbon tetrachloride, 0·85; amyl alcohol, 1·84; absolute alcohol, 2·89; 90% alcohol, 5·58 (large quantities dissolved in the hot solvent separate from the cooled solution until the latter contains 6·4 grams); methyl alcohol, 7·25 (in warm solution, 11·93). Chloroform is the best solvent, the cold solution containing 13·40 and the hot solution 14·84 grams; the bulk of the dissolved substance can be precipitated from its solution in chloroform by addition of ether. Hexamethylenetetramine is insoluble in light petroleum. When obtained from solution and dried in the steam-oven, hexamethylenetetramine is somewhat volatile with the vapour of the solvent, 18·38% of it being removed in forty hours. Determination of the refraction is best effected in aqueous methyl-alcoholic solution.

H. W.

Metallic Compounds of Glycine and Asparagine. II. A. BERNARDI (*Gazzetta*, 1919, **49**, ii, 318—325. Compare A., 1914, i, 1167).—The double *compound* of mercury aminoacetate (compare Ley and Kissel, A., 1899, ii, 485) and mercuric chloride,

$$(NH_2\cdot CH_2\cdot CO_2)_2Hg,HgCl_2,H_2O,$$

prepared from glycine and mercuric chloride in dilute alcohol at 50—60°, forms a white, infusible precipitate, which gradually loses its water of crystallisation in the air.

The double *compound* of mercury asparagine and mercuric sulphate, $[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Hg,HgSO_4$, forms a white, flocculent precipitate and decomposes, without melting, at a high temperature; it is rapidly decomposed in the hot by concentrated potassium hydroxide solution and by ammonia solution, with precipitation of mercury in the former case and of mercuriammonium sulphate in the latter.

The *chromium* compound of asparagine,

$$[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_3Cr,H_2O,$$

prepared from asparagine and chromic acetate, crystallises in tufts of amaranth-red needles, forms an alkaline aqueous solution, and decomposes at about 200°. The *nickel* compound of asparagine, $[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Ni,2H_2O$, prepared from asparagine and nickel hydroxide, crystallises in blue, rectangular plates, has

an alkaline reaction in boiling aqueous solution, and decomposes at above 200°. The *cobalt* compound,

$$[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Co,2H_2O,$$

prepared from asparagine and cobalt hydroxide, crystallises in amaranth-red mamillary masses, shows an alkaline reaction in boiling aqueous solution, and decomposes at above 200°.

T. H. P.

Amino-acids. II. Hydroxyglutamic Acid. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1919, **13**, 398—429).—The author has described previously the isolation of β-hydroxyglutamic acid from the products of hydrolysis of caseinogen (A., 1919, i, 150).

Attempts to synthesise this acid by brominating the acetyl derivative of β-hydroxyglutaric anhydride, and then acting on the bromo-compound with ammonia or by reducing ethyl α-oximinoacetonedicarboxylate, were unsuccessful. Small traces of a substance closely resembling the desired amino-acid were obtained, after some difficulty, by reducing with sodium amalgam the condensation product of orthoformic ester and ethyl oximinoacetonedicarboxylate, and a similar result was obtained by the application of Strecker's method to malic semialdehyde. More satisfactory results were obtained with glutamic acid (I), which was converted into α-carbamidoglutaric acid (II) by the action of potassium cyanate, and hydantoinpropionic acid (III) was obtained from the carbamido-acid by the action of hydrochloric acid. The action of bromine on hydantoinpropionic acid in concentrated solutions in glacial acetic acid gave two products. One would appear to be hydantoin-β-bromopropionic acid (V) and the other hydantoin-βγ-propenylic acid. If the action of bromine is carried out in presence of fuming hydrochloric acid, hydantoin-β-chloropropionic acid (VI) is obtained. The conversion of hydantoin-β-bromopropionic acid into the desired hydroxyglutamic acid was not accomplished with ease. On boiling with water, an unsaturated acid (VII) is obtained, which, on prolonged treatment with hot barium

CO_2H	CO_2H	$CO{-}NH{>}CO$	$CO\cdot NH{>}CO$
$CH\cdot NH_2$	$CH\cdot NH\cdot CO\cdot NH_2$	$CH\cdot NH$	$C{-}NH$
CH_2	CH_2	CH_2	$\Vert$ CH
CH_2	CH_2	CH_2	CH_2
CO_2H	CO_2H	CO_2H	CO_2H
(I.)	(II.)	(III.)	(IV.)
$CO{-}NH{>}CO$	$CO{-}NH{>}CO$	$CO{-}NH{>}CO$	CO_2H
$CH\cdot NH$	$CH\cdot NH$	$CH\cdot NH$	$CH\cdot NH_2$
$CHBr$	$CHCl$	CH	$CH\cdot OH$
CH_2	CH_2	$\Vert$ CH	CH_2
CO_2H	CO_2H	CO_2H	CO_2H
(V.)	(VI.)	(VII.)	(VIII.)

hydroxide solution, is converted into β-hydroxyglutamic acid (VIII). Calculated on the original glutamic acid, the yield is about 2%.

Sufficiently large amounts of the new amino-acid were not obtained to permit of a detailed study, but its properties are all similar to those of the naturally occurring acid isolated from caseinogen. It gives a cherry-red colour with diazobenzenesulphonic acid in the presence of sodium hydroxide, which becomes intensely deep on warming.

Other methods of synthesis were attempted, but were not found practicable. Such were bromination of benzoylglutamic acid with the hope of obtaining benzoylaminoglutaconic acid by removal of hydrobromic acid; reduction of *o*-toluidineazoacetonedicarboxylic ester, and of various hydrazine derivatives of that ester; condensation of oxymethylenehippuric ester with malonic ester; condensation of dichloroacetal with malonic ester, followed by reactions analogous to Leuch's synthesis of serine; reduction of oximinoglutaconic ester and of ethyl hydroxy*iso*oxazoledicarboxylate.

The following compounds are described: *Hydantoin-β-bromopropionic acid*, $C_6H_7O_4N_2Br$ (V), white cubes and rhombic prisms, m. p. 228—230° (decomp.). *Hydantoin-βγ-propenylic acid*, $C_6H_6O_4N_2$ (IV), sulphur-yellow, hexagonal prisms, m. p. 222—223°, solid sublimate being obtained. *Hydantoin-β-chloropropionic acid*, $C_6H_7O_4N_2Cl$, rectangular plates. *Hydantoinacrylic acid* (VII), $C_6H_6O_4N_2$, rosettes of sulphur-yellow needles, m. p. 256—258° (decomp.). β-Hydroxyglutamic acid (VIII), $C_5H_9O_5N$, passes, on heating, into hydroxypyrrolidonecarboxylic acid. Copper salt, very soluble in water, insoluble in alcohol. *Strychnine* salt, $C_{26}H_{31}O_7N_3$, rosettes of needles. Malic semialdehyde, or β-hydroxy-γ-aldehydobutyric acid, $C_4H_6O_4$, did not crystallise; its *semicarbazone*, $C_5H_9O_4N_3$, forms prisms, m. p. 211°; the p-*nitrophenylosazone*,

$$C_{16}H_{14}O_6N_6,$$

m. p. 297—299° (corr.). This compound was identical with the *p*-nitrophenylosazone prepared from the aldehyde produced on the oxidation of the natural hydroxyglutamic acid. β-Hydroxy-γγ-diethoxybutyric acid, $C_8H_{16}O_5$, clear oil, b. p. 120°/5 mm., possesses a sour odour. The *nitrophenylosazone* of the related tartronic semialdehyde, $C_{15}H_{12}O_6N_6$, m. p. 310° (corr.), forms rosettes of fine needles.

β-Hydroxyglutamic acid in 4% solution in water has $[\alpha]_D^{20}$ about ±0·8°, but a 2% solution in hydrochloric acid has $[\alpha]_D^{20}$ +16·3°. The rotation of the potassium salt is practically undetectable, but the addition of uranium nitrate renders it strongly lævorotatory. *Strychnine* d-*β-hydroxyglutamate*, prismatic needles, m. p. 245°, $[\alpha]_D^{20}$ −26·3°. *Brucine* d-*β-hydroxyglutamate*, $C_{28}H_{35}O_9N_3$, needles, decomp. about 200°, $[\alpha]_D^{20}$ −25·0°. *Strychnine* d-*glutamate*, $C_{26}H_{31}O_6N_3$, glistening prisms, m. p. 225—230°, decomp. above 200°, $[\alpha]_D^{20}$ −25·5°. *Brucine* d-*glutamate*, $C_{28}H_{35}O_8N_3,5{\cdot}5H_2O$, m. p. 101°, anhydrous salt, m. p. 240°, stout, prismatic needles with satin lustre, $[\alpha]_D^{20}$ −23°. *Strychnine* l-*aspartate*, $C_{25}H_{29}O_6N_3$,

fine needles, m. p. 252—255°, $[\alpha]_D^{20}$ −28·3°. *Brucine* l-*aspartate*, $C_{27}H_{33}O_8N_3,5H_2O$, fine needles, m. p. 100°; anhydrous salt, m. p. 200°, $[\alpha]_D^{20}$ −28·4°. *Strychnine* l-*α-pyrrolidonecarboxylate*, fan-shaped masses of fine needles, m. p. 245°, $[\alpha]_D^{20}$ −26·7°. *Brucine* l-*α-pyrrolidonecarboxylate*, well-formed prisms, m. p. 180—185°, decomp. above 140°, $[\alpha]_D^{20}$ −31·5°.

β-Hydroxyglutamic acid was isolated to the extent of 2·4% from gliadin and 1·8% from glutein. When administered to the phloridzinised dog, β-hydroxyglutamic acid yields 55—60% of its weight as dextrose, apparently three of its five carbon atoms being concerned in sugar formation. J. C. D.

Preparation of Derivatives of Bromoacylised Carbamide Compounds. FARBENFABRIKEN VORM. F. BAYER & Co. (Brit. Pat. 132795).—On treating bromoacylised carbamide compounds with acylising agents in presence of condensing agents, such as zinc chloride or sulphuric acid, acyl compounds are obtained which have a rapid but lasting sedative and soporific action. Examples are given of the preparation of *acetylbromo-α-ethylbutyrylcarbamide*, m. p. 108—109°, from bromo-α-ethylbutyrylcarbamide (474 parts), acetic anhydride (1000 parts), and zinc chloride (75 parts), the mixture being heated for one hour at 60° and then poured into iced water (3000 parts); of *acetylbromoisovalerylcarbamide*, m. p. 108—109°, from bromo*iso*valerylcarbamide and acetic anhydride: of *propionylbromo-α-ethylbutyrylcarbamide*, m. p. 103°; and of *benzoylbromo-α-ethylbutyrylcarbamide*, m. p. 139—140°, sulphuric acid being employed as condensing agent in each of the last three examples. G. F. M.

Compounds of Univalent Nickel. III. I. BELLUCCI (*Gazzetta*, 1919, **49**, ii. 285—293).—Repetition of the work of Moore (compare A., 1894, i. 102; 1895, ii. 168) yields the following results. When treated in the hot with ammonium chloride solution, ordinary potassium nickelocyanide reacts only in virtue of the potassium cyanide it contains, the nickelous cyanide remaining unchanged: $K_2Ni(CN)_4 + 2NH_4Cl = Ni(CN)_2 + 2KCl + 2NH_4CN$. With the red nickelocyanide (compare A., 1919, i. 526), under similar conditions, two distinct reactions take place: (1) An oxidation, which depends on the marked tendency of the red salt to undergo conversion into the ordinary yellow nickelocyanide, and may follow one of the two schemes, $4K_2Ni(CN)_3 \xrightarrow{2O} 3K_2Ni(CN)_4 + K_2O + NiO$ and

$$4K_2Ni(CN)_3 \xrightarrow{O} 3K_2Ni(CN)_4 + K_2O + Ni.$$

If the reaction is carried out in an inert medium or with the intervention solely of the combined oxygen of the water, as in Moore's experiments, the process of oxidation should proceed mainly according to the second of these two schemes. (2) Precipitation of nickelous cyanide as a result of the action of the ammonium chloride on the yellow potassium nickelocyanide formed in reaction (1). The oxidation (1) proceeds very rapidly, since the

ammonium chloride undergoes gradual hydrolysis and loss of ammonia, the hydrochloric acid thus liberated in the solution uniting with the potassium oxide formed during the oxidation. These conclusions are completely verified by the experimental results.

Moore's supposed suboxide, $Ni_3O,2H_2O$, consists of a mixture of pulverulent metallic nickel with hydrated nickelous oxide, NiO,Aq.

T. H. P.

Preparation of the Tri- and Tetra-carboxylic Esters of Hydrazine and of Ethyl *as*-Hydrazinedicarboxylate. OTTO DIELS and ERICH BORGWARDT (*Ber.*, 1920, **53**, [*B*], 150—158).—*Dicarboxyethylnitroamide* [*ethyl nitroiminodicarboxylate*],

$NO_2 \cdot N(CO_2Et)_2$,

b. p. 115—117°/14 mm., was prepared by the action of ethyl chloroformate on the potassium salt of nitrourethane in boiling toluene solution; attempts to reduce it to ethyl *as*-hydrazinedicarboxylate were unsuccessful, since ethyl iminodicarboxylate was formed with zinc dust in alcoholic solution or with sodium amalgam in moist ether, whilst the action of stannous chloride in ethereal solution in the presence of hydrogen chloride yielded the iminodicarboxylic ester and hydroxylamine hydrochloride. Better results were obtained by acting on the potassium derivative of ethyl benzylidenehydrazinecarboxylate with ethyl chloroformate, whereby *ethyl benzylidenehydrazinedicarboxylate*, $CHPh{:}N \cdot N(CO_2Et)_2$, prisms, m. p. 38—39° after softening at 37°, was obtained, which, when treated with phenylhydrazine in boiling aqueous-alcoholic solution, gave benzaldehydephenylhydrazone and *ethyl as-hydrazinedicarboxylate*, silvery prisms, m. p. 29—30°, b. p. 138—139°/12 mm. (the *hydrochloride*, m. p. 83·5° [? aq.], m. p. 107—108° [after desiccation over phosphoric oxide at 35°], was analysed). The ester was decomposed by distillation under ordinary pressure, yielding ethyl *s*-hydrazinedicarboxylate and a reddish-brown resin; it was converted by *o*-nitrobenzaldehyde into *ethyl o-nitrobenzylidenehydrazinedicarboxylate*, pale yellow crystals, m. p. 26—27°.

Ethyl *as*-hydrazinedicarboxylate was treated with ethyl chloroformate in dry ethereal solution, whereby a mixture of ethyl *as*-hydrazinedicarboxylate and ethyl hydrazinetricarboxylate was formed; the latter was transformed by the successive action of potassium and ethyl chloroformate in toluene solution into *ethyl hydrazinetetracarboxylate*, colourless, highly refractive, viscous oil, b. p. 145—146°/0·65 mm.

The preparation of *ethyl hydrazinetricarboxylate*, colourless, highly refractive oil, b. p. 184—186°/9 mm. (slight decomp.), was effected by the successive action of sodium and ethyl chloroformate on an ethereal solution of ethyl hydrazinecarboxylate (ethyl *s*-hydrazinedicarboxylate, long needles, m. p. 131°, was simultaneously formed), or by the interaction of ethyl chloroformate and ethyl *as*-hydrazinedicarboxylate. Investigation of the ester is not yet completed, but it has been shown that one ester group is readily

eliminated; thus, aqueous potassium hydroxide solution was found to convert it into ethyl *s*-hydrazinedicarboxylate and potassium carbonate,

$$CO_2Et\cdot NH\cdot N(CO_2Et)_2 + H_2O = CO_2 + EtOH + (NH\cdot CO_2Et)_2,$$

whilst propylamine transformed it into a mixture of ethyl *s*-hydrazinedicarboxylate and *dipropylurethane*, colourless, pleasant-smelling liquid, b. p. 83°/10 mm. H. W.

Reduction of Aromatic Nitro-compounds by means of Platinum and Hydrogen. G. Cusmano (*Annali Chim. Appl.*, 1919, **12**, 123—130).—Aromatic nitro-compounds in ethereal solution are rapidly reduced to amines when shaken with platinum-black in an atmosphere of hydrogen. A gradual reduction through nitroso-compounds and hydroxylamines is thus effected in the case of nitroterpenes, whereas in the case of aromatic compounds only a mixture of amines and unaltered nitro-compounds is obtained. The reduction has been found to proceed as shown in the following equations in the case of *p*-nitrophenol, *p*-nitroanisole, *p*-nitrotoluene, *o*-nitrotoluene, and *m*-nitroaniline, although sufficient hydrogen was supplied for the formation of the intermediate nitroso-compounds or β-hydroxylamines:

$$3R\cdot NO_2 + 3H_2 = 2R\cdot NO_2 + R\cdot NH_2 + 2H_2O,$$
$$3R\cdot NO_2 + 6H_2 = R\cdot NO_2 + 2R\cdot NH_2 + 4H_2O.$$

The reduction of certain nitroso-compounds into hydroxylamines follows a similar course. The above-mentioned reactions do not agree with those obtained by reduction with ordinary chemical or electrochemical reagents, which proceed as follows: $R\cdot NO_2 \rightarrow R\cdot NO \rightarrow R\cdot NH_2O \rightarrow R\cdot NH_2$. The nitroso-compounds are always produced in small quantity, but under favourable conditions good yields of the β-hydroxylamines are obtained. β-Hydroxylamines offer more resistance than nitro-compounds to the action of ordinary reducing agents, but are reduced more readily than nitro-compounds by hydrogen and platinum-black. The velocity of the reduction of a β-hydroxylamine depends also on that of its transformation into the tautomeric form containing nitric nitrogen, $R\cdot NH\cdot OH \rightleftarrows O{:}NH_2R$. This transformation may become very rapid when the radicles in the hydroxylamine have no influence on either form, but in acid media, or in the presence of negative radicles tending to stabilise the first (aminic) form, there may be retardation of the reduction, so that the velocity of reduction, from being equal or superior to that of a nitro-compound, may become less than that of the latter. Preliminary experiments have shown that in the case of a mixture of *p*-nitrotoluene and azoxybenzene, the former is preferentially reduced. C. A. M.

Remarkable Instance of Isomerism in the Naphthalene Series. Hartwig Franzen and Fritz Helwert (*Ber.*, 1920, **53**, [*B*], 319—322).—For investigation of the replaceability of the chlorine atoms in chloronitronaphthalenes, the authors have required 1-chloro-4-nitronaphthalene, pale yellow crystals, m. p.

85°, which they have prepared with difficulty in accordance with Atterberg's directions, and have confirmed his results. As, however, the yields are bad, they have also prepared it from 4-nitro-α-naphthamine by Sandmeyer's reaction as modified by Ullmann; in general, the product obtained in this manner was identical with that prepared by nitration of α-chloronaphthalene, but on one occasion, without apparent variation in conditions, the *substance* which was isolated formed yellowish-green crystals, m. p. 60—61°, and gave analytical results agreeing with those required for 1-chloro-4-nitronaphthalene. This is not a case of physical isomerism, since it is not possible to convert the more fusible into the less fusible substance, and since also the two substances yield different *piperidino*-derivatives, yellowish-brown needles, m. p. 70—71°, and yellowish-brown needles, m. p. 63—64°, respectively, whilst also the rates of reaction with piperidine are very different in the two cases. As there appears to be no possible doubt as to the purity and uniformity of the starting materials, an instance of isomerism which is inexplicable by the aid of the generally accepted formula of naphthalene seems to be presented. Unfortunately, it has not been found possible up to the present to repeat the preparation of the isomeride, m. p. 60—61°. H. W.

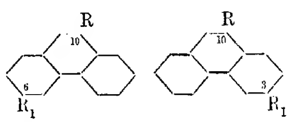
Synthesis of 3 : 10-Dichlorophenanthrene. PAUL NYLÉN (*Ber.*, 1920, **53**, [*B*], 158—167).—The experiments were undertaken with the object of elucidating the constitution of some of the dichlorophenanthrenes obtained by Sandqvist and Hagelin (A., 1919, i, 11); the substance described by these authors as II-10 : 3(6)-dichlorophenanthrene is found to be identical with 3 : 10-dichlorophenanthrene.

α-p-*Chlorophenyl-o-nitrocinnamic acid*, $\begin{array}{l} NO_2\cdot C_6H_4\cdot C\cdot H \\ C_6H_4Cl\cdot C\cdot CO_2H \end{array}$, is best obtained by heating potassium *p*-chlorophenylacetate with *o*-nitrobenzaldehyde and acetic anhydride, filtration from acid potassium acetate, and dilution of the filtrate with a regulated amount of water, whereby the acid is precipitated as pale yellow cubes, m. p. 190·2—190·7° (corr.). (The *ammonium* salt, yellow, lustrous needles, *barium* salt, yellow cubes, and *calcium* salt, prisms, are described.) Further dilution of the filtrates mentioned above yields a further precipitate, from which allo-α-p-*chlorophenyl*-o-*nitrocinnamic acid*, $\begin{array}{l} NO_2\cdot C_6H_4\cdot C\cdot H \\ CO_2H\cdot C\cdot C_6H_4Cl \end{array}$, m. p. 148·5—150° (corr.), is isolated. The substance is characterised as the *allo*-acid by its lower melting point, the greater solubility of its salts (the *ammonium* salt is described), its non-isomerisation by iodine, its sensibility to the action of light, and the formation of a *compound* with aniline, yellow needles, m. p. 124°.

α-p-*Chlorophenyl-o-aminocinnamic acid* is formed in a yellow and a colourless modification, both of which have m. p. 224°, by the reduction of the nitro-acid with ferrous sulphate and ammonia (the *hydrochloride*, *sulphate*, and *ammonium*, *calcium*, and *barium* salts are described), and is transformed by acetic anhydride in the

presence of concentrated sulphuric acid into *β-p-chlorophenyl-carbostyril*, long, colourless needles, m. p. 258·5—259·5° (corr.). Diazotisation converts the amino-acid into *α-p-chlorophenyl-o-diazocinnamic acid*, yellow flocks, which are stable at the ordinary temperature but explode at 101°, from which *3-chlorophenanthrene-10-carboxylic acid*, colourless needles, m. p. 301·5—302·5°, is best obtained by the use of copper powder (the *calcium*, *barium*, *copper*, *iron*, and *silver* salts are described). Distillation under diminished pressure effects the partial conversion of the acid into 3-chlorophenanthrene, m. p. 80—81°, whilst oxidation with chromic acid converts it into 3-chlorophenanthraquinone, yellow needles, m. p. 264·5—265° (corr.) (compare Sandqvist and Hagelin, *loc. cit.*). *Ethyl 3-chlorophenanthrene-10-carboxylate* crystallises in long, colourless, shining needles, m. p. 94·5—95°, and is converted by hydrazine hydrate into the corresponding *hydrazide*, m. p. about 270°, which, with benzaldehyde and acetone, respectively, yields the corresponding *benzylidene* derivative, colourless, prismatic needles, m. p. 248—249° (corr.), and iso*propylidene* derivative, long, colourless needles, m. p. 243—245° (corr.). Diazotisation of the hydrazide is best effected by nitrous fumes, and yields the corresponding *azide*, m. p. about 96° (decomp.). The latter is converted by boiling absolute alcohol into *3-chloro-10-phenanthryl-urethane*, $C_{14}H_8Cl\cdot NH\cdot CO_2Et$, colourless, slender needles, m. p. 197·5° (corr.) after previous softening, which, on treatment with boiling concentrated hydrochloric acid, yields *3-chloro-10-amino-phenanthrene*, pale yellow prisms and needles, m. p. 141·2—142·2° (corr.). [The *hydrochloride*, m. p. about 230°, and the *mono-benzoyl* derivative, colourless, silky needles, m. p. 257·5° (corr.), are described.] Diazotisation of the amine and treatment of the yellow *diazonium* compound with cuprous chloride leads to the formation of 3:10-dichlorophenanthrene, colourless, slender needles, m. p. 117—117·5° (corr.), in rather poor yield. H. W.

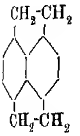
Constitution of Two Series of Doubly Substituted Phenanthrene Derivatives. 3 : 9-Dibromophenanthrene. HÅKAN SANDQVIST (*Ber.*, 1920, **53**, [*B*], 168—171).—In previous communications, several disubstituted phenanthrenes have been described in which one substituent is present in the bridge (say in position 10), the other in position 3 or 6; two genetic series have thus been prepared, which have been provisionally designated I and II. The allocation of the annexed formulæ to the members of the two series is rendered difficult, since the atom in the bridge is affected by oxidation, and the frequently assumed aliphatic character of the linking in the bridge is not such as to allow the ready replacement of the substituting atom by other groups. The synthesis of 3:10-dichlorophenanthrene by Nylén (preceding



abstract) has, however, shown that this substance is identical with II-10 : 3(6)-dichlorophenanthrene obtained by Sandqvist and Hagelin (A., 1919, i, 11), so that all derivatives belonging to the I series are 10:6(=9:3)-compounds, whilst those belonging to the II series are 10:3(=9:6)-substances.

Potassium 10-bromophenanthrene-6-sulphonate is converted by phosphorus pentabromide into 10-*bromophenanthrene*-6-*sulphonyl bromide*, yellow prisms, m. p. 202—203° (slight decomp.), which is converted by further action of the same reagent into 3:9-*dibromophenanthrene*, pale yellow needles and prisms, m. p. 143—143·5°. Chromic acid converts the latter into 3-bromophenanthraquinone. H. W.

The Acenaphthene Series. I. FRITZ MAYER and WALDEMAR KAUFMANN (*Ber.*, 1920, **53**, [*B*], 289—298).—The experiments were undertaken with the twofold object of preparing technically valuable derivatives of acenaphthene and of synthesising *aceacenaphthene* (annexed formula); the latter purpose has not been effected up to the present.



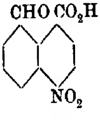
Dibromoacenaphthene tetrabromide, colourless crystals, m. p. 179—180°, is prepared by the addition of a solution of bromine in chloroform to a boiling solution of acenaphthene in the same solvent; it is converted by boiling concentrated alcoholic potassium hydroxide solution into *tetrabromoacenaphthene*, orange crystals, m. p. 180—181°.

5-*Ethylacenaphthene* is obtained as an oil, b. p. ca. 166°/20 mm., 310°/atmos. pressure, by the action of ethyl bromide on acenaphthene in the presence of aluminium chloride. The corresponding *picrate* forms red crystals, m. p. 95—96°. The constitution of the hydrocarbon is deduced from its oxidation through 4-*ethylnaphthalene*-1:8-*dicarboxylic anhydride*, m. p. 180°, to the previously described anhydride of naphthalene-1:4:8-tricarboxylic acid, m. p. 248°. Bromination of 5-ethylacenaphthene gives a yellow oil, b. p. above 170°/vac., which remains unchanged when boiled with an excess of alcoholic potassium hydroxide solution. Distillation of 5-ethylacenaphthene with zinc dust yields acenaphthylene.

5-*Chloroacetylacenaphthene*, m. p. 104°, is prepared by the action of chloroacetyl chloride on the hydrocarbon in the presence of aluminium chloride. Nitration of 5-acetylacenaphthene by nitric acid (D 1·39) in the presence of glacial acetic acid gives ?-*nitro*-5-*acetylacenaphthene*, m. p. 204°. Pyridino-4:5-acenaphthene has m. p. 60—61°, whereas Zinke and Raith (this vol., i, 89) give 67°.

5-*Nitroacenaphthene*-1:2-*quinone* (annexed formula), slender, yellow needles, m. p. 199°, is prepared by the nitration of acenaphthenequinone by concentrated sulphuric acid and nitric acid (D 1·51). (The *mono*- and *di-phenylhydrazones* form dark reddish-brown needles, m. p.

186°, and darker crystals, m. p. 148°, respectively.) The quinone is oxidised by sodium dichromate in the presence of glacial acetic acid to 4-nitronaphthalene-1:8-dicarboxylic acid, the anhydride of which has m. p. 220°. Concentrated potassium hydroxide solution converts the nitroquinone into 4(?5)-nitronaphthaldehydic acid (annexed formula), m. p. 245—247°. 5:6-*Dinitroacenaphthene*-1:2-*quinone*, m. p. above 300° (slow decomp.), is prepared by the more energetic nitration of acenaphthenequinone, and is oxidised by sodium dichromate in boiling glacial acetic acid solution to the *anhydride* of 4:5-*dinitronaphthalene*-1:8-*dicarboxylic acid*, m. p. above 300°; the latter substance (m. p. 310°) appears also to be formed by the oxidation of 5:6-dinitroacenaphthene. H. W.



Preparation of Aromatic Nitro-compounds of Retene and its Homologues. ROBERT ARNOT (D.R.-P. 315623; from *Chem. Zentr.*, 1920, ii, 188—189).—Retene or retenequinone, or a resin oil of high boiling point, particularly tar tallow, is treated with nitric acid (D greater than 1·43) in the presence or absence of fuming sulphuric acid. *Dinitroretene*, from retene or tar tallow and red, fuming nitric acid or concentrated nitric acid (D 1·48—1·52) at 15°, forms a lemon-yellow, flocculent precipitate; the diazonium compound derived from the corresponding amine yields azo-dyes with suitable components. *Dinitroretenequinone*, from the quinone, gives an olive-green solution in alcoholic alkali, which becomes red when warmed and green again when cooled; the hot alcoholic solution of dinitroretenequinone becomes red on addition of alkali. *Nitroretenesulphonic acid*, from retene, 20% oleum, and nitric acid, forms a yellowish-brown precipitate.

H. W.

Fluidities and Volumes of some Nitrogenous Organic Compounds. EUGENE C. BINGHAM, HENRY S. VAN KLOOSTER, and WALTER G. KLEINSPEHN (*J. Physical Chem.*, 1920, **24**, 1—20. Compare A., 1910, ii, 395).—The liquids examined were very carefully purified, and their corrected boiling points are recorded, as follows: benzonitrile 190·7°, *o*-toluidine 198·2°, aniline 182·7°, diethylaniline 212°, dimethylaniline 192·37° (m. p. 2·1°), ethylaniline 203·6°, methylaniline 194·7°, and nitrobenzene 209·3°: these differ in many cases from the generally accepted values. The density and viscosity have been determined at intervals of 10° over the temperature range 0—100°. The experimental results show that aniline is considerably associated: substitution of groups in the benzene nucleus has but little effect on the association, whilst successive substitution in the amino-group reduces the association progressively. The atomic constant for nitrogen in aniline at a fluidity of 200 is 3·4, but it remains an open question whether it has the same value in nitriles and nitro-compounds. Mixtures of aniline and dimethylaniline follow the additive fluidity rule fairly closely. J. F. S.

Trisulphanilic [Aniline-2 : 4 : 6-trisulphonic] Acid. S. C. J. Olivier (*Rec. trav. chim.*, 1920, **39**, 194—199).—When aniline-*p*-sulphonic acid (100 grams) is heated with 600 c.c. of a mixture of one part of phosphoric oxide and three parts of sulphuric acid at 180° for eight hours, *aniline*-2 : 4 : 6-*trisulphonic acid* is obtained and isolated as its *barium* salt, $[C_6H_2(NH_2)(SO_3)_3]_2Ba_3 + 10H_2O$. The free *acid* crystallises with $4H_2O$, is very hygroscopic, and gives a *sodium* salt, $NH_2\cdot C_6H_2(SO_3Na)_3,2H_2O$; a *potassium* salt, $NH_2\cdot C_6H_2(SO_3K)_3,H_2O$, and a *potassium hydrogen* salt,

$$NH_2\cdot C_6H_2(SO_3K)_2\cdot SO_3H.$$

When the acid is diazotised in acid solution with potassium nitrite, or when its potassium salt is diazotised by a current of nitrogen trioxide, it gives a stable diazo-salt, *potassium diazo-benzenetrisulphonate*, $(SO_3K)_2C_6H_2{<}\begin{matrix}N{:}N\\ SO_3\end{matrix}$, which is only slowly decomposed in Gattermann's reaction, giving 1-*chlorobenzene*-2 : 4 : 6-*trisulphonic acid*, yielding an *acid chloride*, $C_6H_2Cl(SO_2Cl)_3$, m. p. 171—171·5°, which, when heated in a sealed tube with phosphorus pentachloride at 200—210° for three hours, yields 1 : 2 : 4 : 6-tetrachlorobenzene.

If anilinetrisulphonic acid itself is diazotised in alcoholic solution with nitrogen trioxide, it yields, after distilling off the alcohol under reduced pressure, *diazobenzenetrisulphonic acid*,

$$\begin{matrix}N{:}N\\ O_3S\end{matrix}{>}C_6H_2(SO_3H)_2,$$

which, when boiled with alcohol, gives benzene-1 : 3 : 5-trisulphonic acid. W. G.

Preparation of Condensation Products from Formaldehyde and Primary Aromatic Amines. Alexander M. Nastukov and Peter M. Croneberg (D.R.-P. 308839; from *Chem. Zentr.*, 1918, ii, 999—1000).—Primary aromatic amines are treated with formaldehyde, preferably in slight excess, in the presence of boiling dilute mineral acids, such as hydrochloric or sulphuric acid; the theoretical yields of amino-bases, free from oxygen and resin and of constant m. p., are thus obtained, which develop on the fibre azo-dyes of red, Bordeaux-red, khaki-brown, or yellow shades. The colours obtained are fast to alkalis, acids, and washing. The *amino-base* from *o*-toluidine, formaldehyde, and sulphuric acid is an amorphous, pale yellow precipitate, m. p. 110—111°. Formaldehyde yields with aniline an amorphous, brownish-yellow *base*, m. p. 114—115°, with technical xylidine a *base*, m. p. 58·5—59·5°, with *o*-anisidine an amorphous, pale yellow *compound*, m. p. 133—134°, and with *m*-toluidine a *base*, m. p. 169—170°. H. W.

Molecular Organic Compounds. III. M. Giua and F. Cherchi (*Gazzetta*, 1919, **49**, ii, 264—285. Compare A., 1917, i, 386).—Investigations have been made on the binary systems formed by diphenylamine with *o*-nitrophenol, *s*-trinitrophenol, azo-

benzene, *n*-cetyl alcohol, 2:4-dichloroaniline, *s*-trichlorophenol, and benzophenone.

The system diphenylamine–*o*-nitrophenol exhibits a single eutectic point at the concentration 51% of the nitrophenol and the m. p. 21·6°. The fused mixtures of the two components show clearly the general phenomenon observed with mixtures of diphenylamine and aliphatic or aromatic nitro-compounds (compare Ciusa and Vecchiotti, A., 1912, i. 755; Pushin and Grebenschtschikov, A., 1913, ii, 105; Tinkler, T., 1913, **103**, 2171; Giua, A., 1915, i. 659; 1916, i, 205; Gomberg and Schoepfle, A., 1917, i, 551), the addition of a small proportion of *o*-nitrophenol sufficing to impart an intense red coloration to diphenylamine.

The results obtained with the system diphenylamine–*s*-trinitrophenol indicate the formation of a compound which contains the components in the molecular ratio 1 : 1, and dissociates on melting. The intense red coloration persists even after solidification of the mixtures, but gradually changes to a greenish-yellow, which is still evident after the solid mass has remained for some days at about 25° (compare Walker, T., 1896, **69**, 1341).

The system diphenylamine–azobenzene exhibits only one eutectic point. The addition of azobenzene in small proportion to diphenylamine results in an intense dark red coloration, but the formation of an additive compound is excluded. The auxochrome group, ·N:N·, of the azobenzene functions, as regards colour, quite similarly to the nitro-group.

Cetyl alcohol, 2:4-dichloroaniline, and *s*-trichlorophenol show no peculiarities in their behaviour towards diphenylamine, the solidification curves possessing one eutectic point in each case. In the cetyl alcohol system, the solidifying point of diphenylamine is lowered from 53·1° to about 38° by addition of 68·99% of the alcohol; mixtures of the two compounds in the hot form pale yellow solutions. For the system diphenylamine–2:4-dichloroaniline, the eutectic corresponds with the concentration 44% of the aniline, and melts at about 44°; fused mixtures of the two components are colourless.

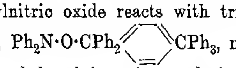
Benzophenone and diphenylamine combine in the molecular proportions 1:1 to form a pale yellow additive compound, m. p. 30·85°, which must be classed with the molecular compounds containing auxochromes (compare Kauffmann, "Die Valenzlehre," Stuttgart, 1911, 509). The eutectic between the additive compound and diphenylamine has m. p. about 28·7°, and that between the compound and benzophenone m. p. about 24°. T. H. P.

Derivatives of Quadrivalent Nitrogen. HEINRICH WIELAND and KARL ROTH (*Ber.*, 1920, **53**, [*B*], 210—230).—The behaviour of diphenylnitric oxide (Wieland and Offenbächer, A., 1914, i, 955) towards other radicles, such as nitric oxide, nitrogen peroxide, triphenylmethyl, and a derivative of diphenylnitrogen, has been investigated, and the unstable di-*p*-tolylnitric oxide has been prepared and examined in a similar direction.

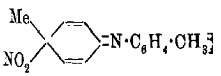
Diphenylhydroxylamine is prepared by a slight modification of the method of Wieland and Roseeu (A., 1912, i, 253), and is transformed into diphenylnitric oxide, m. p. 64° (compare Wieland and Offenbächer, *loc. cit.*), which, when quite pure, can be preserved in ethereal solution during twenty-four hours without undergoing alteration. When its ethereal solution is treated with nitric oxide at 0°, a mixture of *p*-nitrodiphenylnitrosoamine and diphenylnitrosoamine is formed. Apparently the first stage of the reaction consists in the addition of nitric oxide to yield the compound $O{:}NPh_2{\cdot}N{:}O$ (which is analogous to N_2O_3); this probably is converted successively into the isomeric diphenylnitroamine and *p*-nitrodiphenylamine, $Ph_2N{\cdot}NO_2 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NHPh$; the secondary amine is then converted into its nitroso-derivative according to the scheme:

$$NO_2{\cdot}C_6H_4{\cdot}NHPh + O{:}NPh_2{\cdot}N{:}O \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NPh{\cdot}NO + Ph_2N{\cdot}OH.$$

The diphenylamine, which is isolated as its nitroso-derivative, is formed by the auto-decomposition of diphenylhydroxylamine. That a compound analogous in its action to nitrogen trioxide is actually formed is shown by the fact that if the experiment is repeated in the presence of diphenylamine or di-*p*-tolylamine, the nitroso-derivatives of these substances are formed in large quantity.

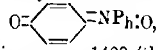
Diphenylnitric oxide reacts with triphenylmethyl to yield the *compound*, , m. p. 160°, the constitution of which is deduced from its catalytic hydrogenation to diphenylamine and the carbinol of Ullmann and Borsum's "hexaphenylethane," which Tschitschibabin (A., 1905, i, 125) has shown to be *p*-benzhydryltetraphenylmethane. The course of the reaction is remarkable, since the simple additive product first formed appears to be so strongly unsaturated that it combines with a second molecule of triphenylmethyl; the hydrogen which is thus liberated reacts with a second molecule of diphenylnitric oxide, so that the molecular ratio 1:1 is preserved, as is experimentally demonstrated to be the case.

Di-p-*tolylnitric oxide*, red needles, m. p. 59—60°, is prepared by oxidising di-*p*-tolylhydroxylamine (Wieland and Roseeu, A., 1915, i, 797) with dry silver oxide; even when placed in a vacuum and removed from light, the substance cannot be preserved for more than three hours; after a few hours it yields a dark, semi-crystalline mass, from which di-*p*-tolylamine can be extracted. With nitric oxide it yields a pale yellow, crystalline, somewhat unstable *compound*, $C_{14}H_{14}O_2N_3$, m. p. 93°, which is not identical with *o*-nitroditolylamine; the substance could not be reduced to ditolylhydrazine or ditolylamine and ammonia, so that it is not ditolylnitroamine. It is provisionally assumed to have the annexed formula.



Di-*p*-tolylhydrazine is converted by nitrogen peroxide into 2:2′-dinitrodi-*p*-tolylamine, cinnabar-red needles, m. p. 192—193° (decomp.).

Di-p-nitrophenylnitric oxide, $(NO_2\cdot C_6H_4)_2N\dot{:}O$, dark red crystals, is prepared by the action of nitrogen peroxide on diphenylnitric oxide, or, more conveniently, on diphenylhydroxylamine. It has m. p. 109° (decomp.) and is remarkably stable, since it can be preserved without change during three months. Its formation probably occurs according to the scheme: $Ph_2N\dot{:}O + NO_2 \longrightarrow O\dot{:}NPh_2\cdot NO_2 \longrightarrow NO_2\cdot C_6H_4\cdot NPh\cdot OH \longrightarrow NO_2\cdot C_6H_4\cdot NPh\dot{:}O \longrightarrow (NO_2\cdot C_6H_4)\cdot NPhO\cdot NO_2 \longrightarrow$
$$(NO_2\cdot C_6H_4)_2N\cdot OH \longrightarrow (NO_2\cdot C_6H_4)_2N\dot{:}O.$$
It is reduced by stannous chloride and hydrochloric acid to 4:4′-diaminodiphenylamine, and by phenylhydrazine to *di-p-nitrophenylhydroxylamine*, orange-yellow needles, m. p. 90° (decomp.); the latter is markedly acidic in character and yields two series of salts, giving, for example, with an ethereal solution of phenylhydrazine a pale orange *compound*, m. p. 126° (decomp.), and with aqueous ammonia or with alkalis intensely deep blue solutions. The use of phenylhydrazine as a reducing agent in this connexion is of particular interest, since other agents transform the oxide directly into the secondary amine. Di-*p*-nitrophenylnitric oxide reacts with nitric oxide to yield a substance which has all the properties expected of *di-p-nitrophenylnitroamine*; it is, however, decomposed by crystallisation from ethyl acetate, yielding 4:4′-dinitrodiphenylamine, m. p. 213—215°; it combines with triphenylmethyl to yield *NN-di-p-nitrophenyl-O-triphenylmethylhydroxylamine*, $(O_2N\cdot C_6H_4)_2N\cdot O\cdot CPh_3$, pale yellow, rhombic platelets, m. p. 180° (decomp.), which is reduced by hydrogen in the presence of palladium-black to 4:4′-diaminodiphenylamine and triphenylcarbinol.

Diphenylnitric oxide is remarkably stable towards water and alkalis, but is rapidly converted by 2*N*-hydrochloric acid into diphenylamine and *quinoneanil oxide*, , shining prisms with a pale brown surface coloration, m. p. 142° (the latter is reduced by zinc dust in glacial acetic acid solution to *p*-hydroxydiphenylamine, which is converted by dry silver oxide into quinoneanil, m. p. 98°). For some unexplained reason, ethereal solutions of diphenylnitric oxide occasionally undergo the same change spontaneously.

The stability of the diarylnitric oxide diminishes from the dinitrophenyl through the phenyl to the di-*p*-tolyl derivative; the stability of the di-*p*-anisyl compound described by Meyer and Gottlieb-Billroth (this vol., i, 38) is therefore remarkable. H. W.

The Transformation of Dinitrophenolsulphonic Acids into Picric Acid. M. Marqueyrol, P. Carré, and P. Loriette (*Bull. Soc. chim.*, 1920, [iv], **27**, 140—143).—The transformation of 2:6-dinitrophenol-*p*-sulphonic acid into picric acid is more rapid

than that of the 2:4-dinitrophenol-*o*-sulphonic acid. It is thus preferable, in the manufacture of picric acid, to use a sulphonated phenol mixture containing the maximum amount of phenol-2:4-disulphonic acid. W. G.

The Preparation of Picric Acid by the Process with Nitric Acid using Nitric Acids of Different Concentrations. M. Marqueyrol, P. Carré, and P. Loriette (*Bull. Soc. chim.*, 1920, [iv], **27**, 143—148).—By arranging completely to utilise the nitric acid used, it is possible to obtain good yields of picric acid by sulphonating 100 grams of phenol with 350 grams of 92·5% sulphuric acid, heating the mixture on a water-bath for three hours, and then nitrating the mixture with five molecular proportions of nitric acid (D 1·273). Under laboratory conditions, it does not seem possible to use less than these proportions of sulphuric and nitric acids. W. G.

Equilibrium Diagrams of Binary Mixtures of Picric Acid, Trinitrotoluene, Dinitrotoluene, and Mononitronaphthalene. A. Wogrinz and P. Vári (*Z. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 249—251, 267—270; from *Chem. Zentr.*, 1920, i, 115).—The cooling curves have been deduced from experiments performed in a special type of apparatus, which is fully described, and is designed to secure closely similar external conditions. The curves are given for the systems: picric acid–dinitrotoluene, tri- and di-nitrotoluenes, trinitrotoluene–nitronaphthalene. H. W.

Modern Shattering Nitro-explosives. C. F. van Duin and B. C. Roeters van Lennep (*Rec. trav. chim.*, 1920, **39**, 145—177).—The authors have examined nineteen nitro-compounds of different types, capable of being used as explosives, to determine their stability, temperature of explosion, and sensitiveness to mechanical shock, and thus to determine the influence of constitution on these properties.

For the stability test, the Dutch method has been used, which consists in heating 10 grams of the substance in a special flask at 95° first for three hours, and if no decomposition occurs, for eight hours per day up to a period of thirty days. Under these conditions, trinitrophenylmethylnitroamine, trinitroaminophenol, trinitroaminoanisole, trinitroaminophenetole, trinitro-*m*-phenylenediamine, trinitromethylnitroaminophenol, aminotrinitrophenylmethylnitroamine, hexanitrodiphenyl sulphide and sulphone, and dipicrylamine stood the test. Tetranitroaniline showed marked decomposition after twenty-six hours at 60°, whilst tetranitrophenylmethylnitroamine was even less stable, the substance containing the most active nitro-group being thus the least stable. Tetranitrophenol showed signs of decomposition after four hours at 70°. In general, the 2:3:4:6-tetranitro-derivatives decompose rapidly either at high temperatures or at the ordinary temperature, this being probably due to the splitting off of the nitro-group in

position 3. Stettbacher's view (compare *Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 114) that the nitrous acid evolved in the decomposition of tetranitroaniline comes from an action between the amino- and the *o*-nitro-groups is incorrect. The instability of substances with mobile nitro-groups is due to these mobile groups, and a methylnitroamino-group also exerts an unfavourable influence on the stability of a compound.

In determining the temperature of explosion, it is advisable to determine the figure by two methods, one in which the temperature is raised above 100° by 20° a minute, and the second in which it is only raised 5° a minute, in order to get a correct idea of the behaviour of the explosives. There is apparently no definite relationship between the explosion temperature and the stability of a compound. In the case of substances which decompose at their melting point, the decomposition and explosion temperatures are generally almost equal.

For testing such nitro-explosives for their sensitiveness to shock, the authors find Kast's method (compare *Z. ges. Schiess. u. Sprengstoffw.*, 1909, **4**, 263) quite satisfactory. The introduction of a methylnitroamino-group or of a fourth nitro-group notably increases the sensitiveness to shock, whilst an amino-group lowers it. The etherification of a phenol diminishes its sensitiveness. Apart from the nature of an entrant group, its mobility, in the case of highly nitrated substances, exerts a marked influence, mobility increasing sensitiveness. The replacement of a fixed nitro-group by a mobile group produces a remarkable influence on the sensitiveness, as is shown by a comparison of dipicrylamine with 2:4:6:2′:3′:4′-hexanitrodiphenylamine. W. G.

Esters of *N*-Arylsulphonyl-*N*-alkylaminoaryl Esters. E. REBER and J. SIEGWART (U.S. Pat. 1316804).—*N*-Toluenesulphonyl-*p*-aminophenyl toluenesulphonate (*A*),

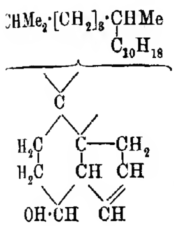
$$C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_4Me,$$

is dissolved in aqueous sodium hydroxide, and, on cooling the hot solution, the sodio-derivative crystallises. This is converted almost quantitatively into the N-*methyl* derivative of *A*, needles, m. p. 162°, by heating for several hours at 100—120° with methyl chloride and methyl alcohol. Other alkylating agents may be used, such as ethyl haloids (m. p. 117°), allyl bromide (m. p. 113°), ethylene dibromide, or benzyl bromide (m. p. 142°), with alcohol or water as diluent (the m. p. of the derivative of *A* produced is given in brackets). Corresponding derivatives of *o*- or *m*-aminophenol, or of the aminonaphthols and their substitution products, which are substituted in the amino-group by an arylsulphonyl radicle and in the hydroxyl group by an acyl radicle, can also be easily alkylated. CHEMICAL ABSTRACTS.

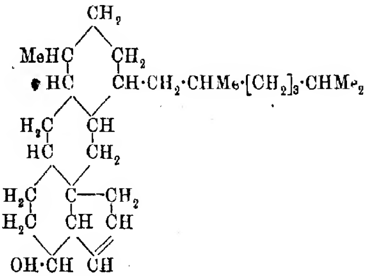
Catechol. BENNO ELSNER (*Monatsh.*, 1919, **40**, 361—362).—At dilutions not greater than 1%, with excess of cold barium hydroxide solution, catechol gives a precipitate of a very sparingly

oluble *barium* salt, $C_6H_4O_2Ba,3\frac{1}{2}H_2O$, in the form of silver-grey eaflets with a pearly lustre. Since resorcinol and quinol do not ive such a precipitate, the reaction is suggested as a means of eparation, which is probably superior to that which depends on he use of benzene. J. K.

Constitution of Cholesterol. A. Windaus (*Nachr. K. Ges. Wiss. Göttingen*, 1919, 237—254; from *Chem. Zentr.*, 1920, i, 82). —The author gives a general account of the investigations which have, in part, served to elucidate the constitution of cholesterol. In comparison with the formulæ of the original communications, the present formulæ are increased by the addition of two atoms of hydrogen, since this alteration has been shown to be necessary for the acid, $C_{26}H_{44}O_3$, obtained by the oxidation of cholestenone by potassium permanganate (compare A., 1917, i, 265). If the presence of an octyl radicle (Windaus and Resau, A., 1913, i, 615) be regarded as established, the constitution of cholesterol may be expressed by formula I:



(I)



(II)

Two saturated ring systems must be present in the residue which contains ten carbon atoms, and these probably have certain carbon atoms in common with the rings of formula I. Although complete evidence with regard to certain details is lacking, it is possible to put forward a constitutional formula which gives an approximately accurate picture of the arrangement of the carbon atoms. A possible constitution is shown by formula II. H. W.

Solubility of Microbic Acid [*p*-Chlorobenzoic Acid]. R. Otto (*Konserven Zeit*, 1917, **18**, No. 1; *Landw. Jahrb.*, **52**; *Erg. Bd.* **1**, 85—86; from *Chem. Zentr.*, 1919, iii, 1052—1053). —The solubility of *p*-chlorobenzoic acid is given by Seeger as 1:2500 and by Beilstein as 1:5288; the author finds the acid to be much more sparingly soluble than these figures would indicate, and that 25,000 parts of water do not completely dissolve 1 part of it. Failure to detect the presence of *p*-chlorobenzoic acid in alcohol-free fruit juices which have been treated with microbin is therefore readily explicable. H. W.

Catalytic Preparation of Amides. A. MAILHE and (MME) BELLEGARDE (*Caoutchouc et Guttapercha*, 1919, **16**, 9947—9948; from *Chem. Zentr.*, 1919, iii, 952).—Although aromatic amines react readily with aliphatic and aromatic acids to yield substituted amines, the esters, such as methyl benzoate, can be boiled with aniline for a protracted period without forming an appreciable amount of the amide. It is now shown that substituted amines may be readily produced when an equimolecular mixture of ester and amine is allowed to react in the presence of aluminium oxide or thorium oxide at 480—490°. Amides, but not nitriles, are obtained when a mixture of ammonia and the vapour of an acid anhydride is passed over the same catalysts at 450°, and a similar change is observed when an ester is used in place of the anhydride. At a higher temperature, larger amounts of nitriles are produced in certain circumstances. The following examples are cited. Benzanilide is prepared from aniline and methyl or ethyl benzoate, the yield being 40—50% of the quantity of ester used; the three isomeric benzotoluidides from benzoic ester and the requisite toluidine; *benzo*cyclo*hexylamide*, $C_6H_{11}\cdot NH\cdot COPh$, m. p. 153°, from methyl benzoate and *cyclo*hexylamine; phenylpropionanilide; cuminanilide; acetanilide and its homologues from aniline and the corresponding aliphatic esters. The following compounds are obtained by the use of gaseous ammonia. Propionamide and *iso*valeramide from the corresponding anhydrides; salicylamide from methyl salicylate (in this instance the formation of nitrile is not observed if the catalyst is heated to 500°). H. W.

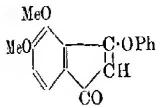
Preparation of New Mono- and Di-β-hydroxyethylaminobenzoic Esters. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 128552).—Mono- and di-β-hydroxyethylaminobenzoic esters are obtained by heating to temperatures varying from 50° to 110° a mixture of ethylene oxide and an aminobenzoic ester in molecular proportion of one or two of ethylene oxide respectively to one of ester. The reaction can be accelerated by the addition of small quantities of water or ethyl alcohol. Thus *ethyl β-hydroxyethyl*-p-*aminobenzoate*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Et$, a colourless, crystalline substance, melting at 63° and boiling at 213—214°/4 mm., is produced by heating for several hours in a closed vessel at 50° equimolecular proportions of ethylene oxide and ethyl *p*-aminobenzoate, whilst if under similar conditions 2 mols. of ethylene oxide are used, together with ½ mol. of water and 1 mol. of ethyl alcohol, *ethyl di-β-hydroxyethyl*-p-*aminobenzoate*,

$$(OH\cdot CH_2\cdot CH_2)_2N\cdot C_6H_4\cdot CO_2Et,$$

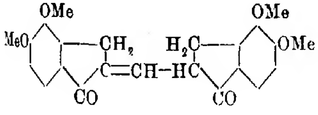
is obtained. After crystallisation from benzene it forms white lamellæ, m. p. 94° and b. p. 246°/4 mm. G. F. M.

2 : 3-Dimethoxyphenylpropiolic Acid and 4 : 5-Dimethoxyhydrindone. S. RUHEMANN (*Ber.*, 1920, **53**, [*B*], 274—284).—Ethyl 2:3-dimethoxycinnamate (compare Perkin and Robinson, T., 1914, **105**, 2387; Kranichfeldt, A., 1914, i, 190), colourless

prisms, m. p. 45—46°, b. p. 184—185°/15 mm., is prepared by the action of ethyl acetate and sodium on 2:3-dimethoxybenzaldehyde; it readily absorbs bromine to yield the corresponding dibromo-ester, but, at the same time, a certain amount of hydrogen bromide is invariably eliminated. The crude ester, which could not be purified, is converted by alcoholic potassium hydroxide solution into 2:3-*dimethoxyphenylpropiolic acid*, $C_6H_3(OMe)_2{\cdot}C{:}C{\cdot}CO_2H$, colourless prisms, m. p. 108—109°. In a similar manner to 4-methoxy-1-naphthylpropiolic acid (this vol., i, 326), the latter is transformed by alcohol and hydrogen chloride into *ethyl β-chloro-2:3-dimethoxycinnamate*, colourless oil, b. p. 190—191°/12 mm., which, when treated with sodium phenoxide, gives *ethyl β-phenoxy-2:3-dimethoxycinnamate*, pale yellow, viscous oil, b. p. 242—244°/12 mm. Hydrolysis of the latter yields the two stereoisomeric *β-phenoxy-2:3-dimethoxycinnamic acids*, coarse, colourless crystals, m. p. 192—193° (decomp.), and silky needles, m. p. 137—138°, respectively, which can be comparatively readily separated by fractional crystallisation from alcohol. Instead of the expected flavone, either isomeride, when acted on by phosphorus pentachloride and aluminium chloride successively, yields 3-*phenoxy-4:5-dimethoxyindone* (annexed formula), colourless, shining leaflets, m. p. 199—200°, the constitution of which is deduced from its conversion by hydriodic acid into phenol and 4 : 5-*dihydroxyindane*-1 : 3-*dione*, colourless needles, m. p. 277—278° (decomp.), the white, unstable *silver* salt of which is also described.

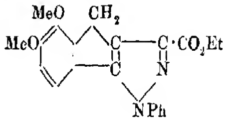


4:5-Dimethoxy-1-hydrindone, yellow leaflets, m. p. 77—78° (Perkin and Robinson, T., 1914, **105**, 2388, give 82°), is conveniently prepared from 2:3-dimethoxy-β-phenylpropionic acid by the successive action of phosphorus pentachloride and aluminium chloride. Attempts to convert it into an azomethine by the action of *p*-nitrodimethylaniline and potassium hydroxide were unsuccessful, the alkali affecting almost exclusively the nitroso-base and forming pp′-*tetramethyldiaminoazoxybenzene*, yellowish-brown needles, m. p. 239—240°. 4:5-*Dimethoxy-2-hydroxymethylene*-1-*hydrindone*, almost colourless needles, m. p. 135—136°, after softening at 130°, is prepared by the action of sodium and ethyl formate on the hydrindone; the *copper* salt, greenish-yellow powder, and the *anilide*, $C_{11}H_{10}O_3{:}CH{\cdot}NHPh$, yellow prisms, m. p. 168°, are described. When the hydroxymethylene compound is heated at 160° it loses formic acid and yields a *compound* (annexed formula), red prisms, m. p. 222°.



Ethyl oxalate condenses with 4:5-dimethoxy-1-hydrindone in the presence of sodium ethoxide, yielding *ethyl* 4:5-*dimethoxy*-1-

hydrindoneglyoxylate, yellow needles, m. p. 132—133°, from which the corresponding *acid*, yellow needles, m. p. 232°, is obtained in the usual manner. The ester reacts readily with phenylhydrazine hydrochloride in the presence of a few drops of concentrated hydrochloric acid, giving *ethyl* 7 : 8-*dimethoxy-1-phenylindeno-2′ : 3′ : 4 : 5-pyrazole-3-carboxylate* (annexed formula), colourless, silky needles, m. p. 172—173°; the corresponding acid forms slender needles, m. p. 240—241° (decomp.). H. W.



Ethyl Diphenyleneacetate. S. RUHEMANN (*Ber.*, 1920, **53**, [*B*], 287—289).—The sodio-derivative of ethyl fluorene-9-dicarboxylate (Wislicenus and Mocker, A., 1913, i, 1187) reacts with ethyl phenylpropiolate to yield carbon dioxide and *ethyl β-diphenylenemethylcinnamate*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CH\cdot CPh\!:\!CH\cdot CO_2Et$, yellow crystals, m. p. 98—99°; the corresponding *acid* crystallises in yellow leaflets, m. p. 219—220°, and is reduced by sodium amalgam to *β-diphenylenemethyl-β-phenylpropionic acid*, colourless prisms, m. p. 184—185°. H. W.

Regularities Observed in the Pyrogenic Degradation of certain Cyclic Hydroxy-acids of the Benzene Series. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber.*, 1920, **53**, [*B*], 190—201).—When salicylic acid is rapidly heated to a temperature not exceeding 250°, it loses carbon dioxide and water, but only 46·39% of it is converted into phenyl salicylate; at temperatures between 250° and 350°, carbon dioxide is evolved in regularly increasing amount, and, above 280°, the formation of phenol in small quantity can be detected. When rapidly distilled, the acid (contrary to the generally accepted views) does not undergo an even partial, smooth conversion into carbon dioxide and phenol; the product only contains very small quantities of the latter in addition to salol and other substances. Similar experiments with protocatechuic acid (3 : 4-dihydroxybenzoic acid) show that a smooth decomposition into catechol and carbon dioxide does not occur between 200° and 300°. Rapid distillation of protocatechuic acid yields carbon dioxide, catechol, and tetrahydroxyanthraquinone (rufiopine). Gallic acid, on the other hand, is quantitatively converted at 240—245° into carbon dioxide and pyrogallol or Pelouze's melangallic acid; when rapidly distilled it yields 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone. The formation of derivatives of anthracene from benzene compounds by a purely pyrogenic action is of interest in that it affords a possible explanation of the occurrence of compounds of the two series in coal tar. H. W.

Syntheses of Naphthyl-lactic and Naphthylcinnamic Acids. II. β-Phenyl-β-2-naphthyl-lactic Acid. REMO DE FAZI (*Gazzetta*, 1919, **49**, ii, 250—253. Compare A., 1919, i, 529).—*β-Phenyl-β-2-*

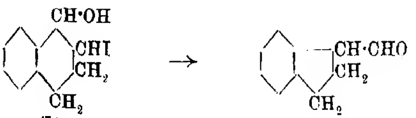
naphthyl-lactic acid, $C_{10}H_7 \cdot CPh(OH) \cdot CH_2 \cdot CO_2H$, obtained as ethyl ester by decomposing by means of acidified water the complex formed by the interaction of phenyl β-naphthyl ketone and ethyl bromoacetate in benzene solution in presence of zinc dust, forms slender, white needles, m. p. 225—226°, and with concentrated sulphuric acid gives an emerald-green coloration, which immediately changes to yellowish-brown with intense green fluorescence. The *ethyl* ester forms white laminæ, m. p. 114—115°, and with concentrated sulphuric acid gives an intensely green solution showing marked green fluorescence. T. H. P.

Phthaleins and Fluorans. MAURICE COPISAROW (T., 1920, 117, 209—218).

Preparation of *p*-Dimethylaminobenzaldehyde. T. INGVALDSEN and L. BAUMAN (*J. Biol. Chem.*, 1920, **41**, 145—146).—The authors modify the method of Ullmann and Frey (A., 1904, i, 423) by omitting the isolation of the hydrochloride of the benzylidene compound prepared by the condensation of *p*-nitrosodimethylaniline and *p*-dimethylaminobenzyl alcohol, and decomposing the free base by formaldehyde and acetic acid at the ordinary temperature. The crude aldehyde is purified by distillation in a partial vacuum. J. C. D.

The Iodhydrin Derived from Cinnamyl Methyl Ether. HENRI BEAUFOUR (*Bull. Soc. chim.*, 1920, [iv], **27**, 148—152. Compare A., 1912, i, 621; 1913, i, 466, 467).—The iodohydrin obtained by treating cinnamyl methyl ether with iodine and mercuric oxide (*loc. cit.*), when slowly added in ethereal solution to an aqueous solution of silver nitrate (compare Tiffeneau, A., 1907, i, 922), gives *methyltropaldehyde*, $OMe \cdot CH_2 \cdot CHPh \cdot CHO$, b. p. 217—218°, D^0 1·0711, giving an *oxime*, b. p. 175°/15 mm., D^0 1·121, and a *semicarbazone*, m. p. 125°. On oxidation it yields *methyltropic acid*, m. p. 63°, b. p. 177—180°/15 mm., giving an *ethyl* ester, b. p. 139—140°/10 mm. or 250—251°/765 mm., D^0 1·0724. Attempts to prepare the corresponding primary alcohol by reduction of this ester were not successful, the main product, in every case, being atropic acid. W. G.

Phenylic Transposition in the Tetrahydronaphthalene Series. M. TIFFENEAU and A. ORÉKHOFF (*Compt. rend.*, 1920, **170**, 465—467).—The iodhydrin of αβ-tetrahydronaphthalene glycol (I), when treated with silver nitrate in ethereal solution, undergoes phenylic transposition, giving *hydrindene-2-aldehyd-*



(I.) (II.)

(formula II), b. p. 135°/30 mm., D^0 1·095, giving a *semicarbazone*, m. p. 167°, an *oxime*, m. p. 104°, and a *bisulphite* compound.

Neither the iodhydrin of ββ-tetrahydronaphthalene glycol nor the iodhydrin of hydrindene glycol undergoes this transposition when similarly treated with silver nitrate. W. G.

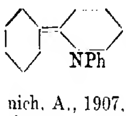
The Beckmann Rearrangement. IX. Action of Phosphorus Pentasulphide on Benzophenoneoxime. MITSURU KUHARA and KÔZÔ KASHIMA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1919, **4**, 69—75. Compare A., 1918, i, 179).—Dodge (A., 1891, 1238) and Ciusa (A., 1906, i, 953) have observed that thiobenzanilide is formed when benzophenoneoxime is warmed with phosphorus pentasulphide, and have ascribed this change to the Beckmann rearrangement of thiobenzophenoneoxime, formed according to the equation $5CPh_2\colon N\cdot OH + P_2S_5 = 5CPh_2\colon N\cdot SH + P_2O_5$. In analogy with Kuhara's previous studies of this transformation, it is now found that the rearrangement is due to the formation of an ester of the thio-oxime, for when the reaction is carried out in ethereal suspension, *thiobenzophenoneoxime hydrogen phosphate*, $OH\cdot PO(SN\colon CPh_2)_2$, is obtained as a fibrous, greenish-yellow mass, which changes into thiobenzanilide with almost explosive violence at 70°. A more stable derivative is obtained by treating this ester with cold, alcoholic potassium hydroxide, the product being *thiobenzophenoneoxime dipotassium hydrogen orthophosphate*,

$$OH\cdot PO(OK)_2(SN\colon CPh_2)_2,$$

a white, crystalline powder which changes into thiobenzanilide at 149°. J. C. W.

Zinc Chloride as a Condensing Agent. V. Condensation Products of Aniline and Hydroaromatic Ketones. G. REDDELIEN and O. MEYN (*Ber.*, 1920, **53**, [*B*], 345—354. Compare A., 1914, i, 698, and following abstract).—It has been shown previously that aniline zincichloride powerfully catalyses the condensation of ketones with amines, and is the only useful agent in the cases of enolisable ketones containing the group $\cdot CO\cdot CH_2\cdot$ and of unsaturated ketones of the type $>C\colon C\colon CO$. It is now found to be applicable to hydroaromatic ketones.

cyclo*Hexanoneanil*, pale yellow oil, b. p. 140°/19 mm., is obtained by heating *cyclo*hexanone, aniline, and aniline zincichloride at 155° during twenty minutes; with other condensing agents, such as aniline hydrochloride, extensive auto-condensation and considerable resinification take place, and non-uniform products of very high boiling point are formed. *cyclo*Hexanoneanil is a reactive substance which undergoes auto-condensation, yielding the *substance*, $C_{18}H_{23}N$, b. p. 212—214°/18 mm., which is regarded as cyclo*hexylidene*-2-cyclo*hexanoneanil* (annexed formula), since, when treated with dilute acids, it gives aniline and *cyclo*hexylidene-2-*cyclo*hexanone (compare Wallach, A., 1907, i, 220; Mannich, A., 1907, i, 205). The condensed anil is the main product of the action of aniline on *cyclo*hexanone in the presence of aniline



zincichloride at 180° for three-quarters of an hour, and can also be prepared by heating *cyclo*hexanoneanil with aniline hydrochloride for a few minutes at 200°. At a higher temperature it also undergoes auto-condensation, and yields aniline and an *anil*, possibly $C_{18}H_{26}$:NPh, dark yellow oil, b. p. 240—250°/14 mm.

Similarly, menthone yields *menthoneanil*, yellow oil, b. p. 159—160°/12 mm.; *menthone*-p-*toluil*, yellow oil, b. p. 178°/16 mm.; and *menthone*-p-*anisil*, colourless crystals, m. p. 61·5°, b. p. 195°/16 mm. These substances cannot be preserved for any length of time in contact with air, since they become oxidised and darken in colour. Condensing agents other than aniline zincichloride yield dark brown, resinous oils.

Among unsaturated hydroaromatic ketones, pulegone yields a normal *anil*, yellow oil, b. p. 148—152°/12 mm., and, in addition, 7-*anilinomenthone*, b. p. 154—158°/13 mm., and 7-*anilinomenthoneanil*, b. p. 153—156°/18 mm.; the latter substances are probably formed by simple addition of aniline to pulegone and pulegoneanil respectively by a process which is not infrequently associated with the action of amines on substances having conjugated double bonds. Dihydrocarvone, on the other hand, yields the *anil*, yellow oil, b. p. 170—171°, very smoothly and without noticeable formation of by-products. *Carvoneanil*, pale yellow oil, b. p. 180—182°/17 mm., is remarkably readily prepared, reaction occurring to some extent between the components at 160° in the absence of catalyst. Camphor, on the other hand, did not react with aniline itself, and only to a small extent in the presence of aniline zincichloride; *camphoranil*, yellow oil, b. p. 164·5—166°/15 mm., m. p. 13·5°, could be obtained in 64% yield by the use of aniline hydrochloride as condensing agent.

Solution of the anils of the unsaturated hydroaromatic ketones in concentrated sulphuric acid gives an intense blue coloration with nitric acid. The reaction is as sensitive as the brucine test. It is shown by carvoneanil, pulegoneanil, and dihydrocarvoneanil (in order of decreasing sensitiveness), but not by *cyclo*hexanoneanil, menthoneanil, or camphoranil. The action thus appears to depend on the presence of the group >C:C·C:NPh. The presence of the anil group is shown to be essential, since the coloration is not given by carvonephenylhydrazone. Nitrite, chlorate, chromate, and hydrogen peroxide also yield the colour, which therefore depends on oxidation.

H. W.

Condensation Products from Benzylamine and Aromatic Ketones. G. REDDELIEN (*Ber.*, 1920, **53**, [*B*], 334—340).—It has been shown previously (A., 1913, i, 1203) that hydrogen haloids are frequently effective catalysts in promoting the action of aromatic ketones with amines to form ketoneanils; it is now shown that benzophenonebenzylimide, CPh_2:N·CH_2Ph, m. p. 60—61°, is readily obtained from benzophenone and benzylamine at 180° in the presence of a few drops of hydrobromic acid solution; Hantzsch and Hornbostel (A., 1898, i, 195) have previously prepared the same

substance from benzophenone dichloride, since they found that the ketone and amine did not react to an appreciable extent with one another even at an elevated temperature. Acetophenonebenzylimide, transparent needles, m. p. 44·5°, can be obtained in improved yield from the ketone and amine by a slight modification of the procedure of Hantzsch and Hornbostel (*loc. cit.*); when, however, the condensation is effected in the presence of $ZnCl_2,2NH_3$ or hydrobromic acid an entirely different substance is obtained, which is identified as 2:4:6-triphenylpyridine, and is shown to be identical with the product prepared from benzylidenediacetophenone and hydroxylamine by Wislicenus and Newmann (A., 1899, i, 61), from acetophenone and ammonia in the presence of phosphoric oxide (Engler and Heine, this Journ., 1873, 1036; Riehm, A., 1887, 599), and by the distillation of acetophenone ammonia (Thomas, A., 1907, i, 138). The substance behaves as a very feeble base, but, when crystallised from concentrated hydrochloric acid, gives a *hydrochloride*, which somewhat rapidly loses hydrogen chloride when preserved; it separates as unchanged base from its solution in more dilute acid. The formation of triphenylpyridine from acetophenonebenzylimide is accompanied by that of benzylamine or dibenzylamine and methane. H. W.

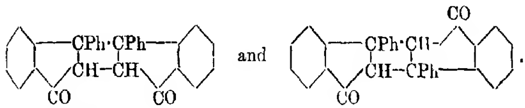
Catalytic Action of Hydrogen Haloids in Condensations. II. The Decomposition of Anils. G. Reddelien (*Ber.*, 1920, **53**, [*B*], 355—358).—It has been shown previously (A., 1913, i, 1203) that hydrogen haloids are effective catalysts in the formation of anils from ketones and aniline, and emphasis has been laid on the necessity of a vigilant control of the temperature of the reaction if the formation of by-products in large amounts is to be avoided. Further investigation now shows that the anils are decomposed when heated with aniline hydrobromide. Thus, benzylideneaniline, when distilled with the addition of a small quantity of dry aniline hydrobromide, gave aniline, toluene, and acridine, in addition to much brown, resinous matter. A somewhat similar behaviour was observed with fluorenoneanil and benzildianil, which evolved aniline at above 200°; benzophenoneanil, on the other hand, appeared to be stable.

The possibility of utilising the elimination of aniline for the condensation of anils with reactive hydrocarbons has also been investigated. Benzophenoneanil and diphenylmethane scarcely reacted with one another. Benzophenoneanil and fluorene did not react below 300°, but, after addition of a small quantity of aniline hydrobromide, aniline was readily evolved at 270°, and a hydrocarbon was obtained which was identified as bisdiphenylene-ethane instead of the expected diphenyldiphenylene-ethylene, whilst bisdiphenylene ethylene was also formed in minor quantity. Fluorenoneanil and fluorene yielded a similar mixture of hydrocarbons.

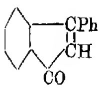
H. W.

Indones. III. 3-Phenylindone and Diphenyltruxones. Remo de Fazi (*Gazzetta*, 1919, **49**, ii, 253—263. Compare A., 1915, i, 1063; 1916, i, 151).—$\beta\beta$-Diphenyl-lactic acid does not give

3-phenylindone when treated with phosphoric oxide, but its ethyl ester yields with sulphuric acid the emerald-green coloration regarded by the author as characteristic of those derivatives of lactic and cinnamic acids which are capable of furnishing indones. The green solution is found to contain: (1) a small proportion of an orange-red compound which, in acetic acid solution containing palladium-black, absorbs hydrogen forming 3-phenylhydrindone, and must therefore be 3-phenylindone; (2) considerable proportions of two colourless compounds, $C_{30}H_{20}O_2$, which are dimerides of 3-phenylindone, do not combine with chlorine or bromine, and give no coloration with sulphuric acid; they are therefore regarded as isomeric diphenyltruxones (compare Liebermann, A., 1898, i, 662), having the probable constitutions:



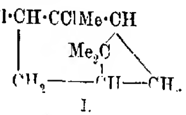
3-Phenylindone (annexed formula) forms an orange-red powder, m. p. 69—71°, and gives an emerald-green coloration with sulphuric acid.



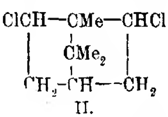
The two *diphenyltruxones* form (1) large, cubical crystals, m. p. 252—253°, and (2) shining, transparent, white prisms, m. p. 209—211°. Both have the normal molecular weights in boiling chloroform. In acetic acid or alcoholic solution, isomeride (2) does not absorb hydrogen in presence of palladium-black, but in acetic acid isomeride (1) slowly absorbs hydrogen, giving a *compound*, $C_{30}H_{24}O_2$, which forms shining, white scales and does not melt at 275°; in this compound the two carbonyl groups of the diphenyltruxone are converted into CH(OH) groups. T. H. P.

Some Derivatives of Fisetol. WILLIAM KERSHAW SLATER and HENRY STEPHEN (T., 1920, **117**, 309—319).

Chlorination of Pinene. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1915, **57**, 14 pp.; from *Chem. Zentr.*, 1918, ii, 952—953).—The chlorination of pinene in the absence of moisture at −15° to 0° has been investigated; the results differ from any previously recorded. Chlorination occurs in a highly complex manner. The first fractions of the product give abundant solid deposits of pinene hydrochloride. From the higher fractions only a *pinene dichloride* (? II) was obtained, which may have been formed from a primary,



I.



II.

*m**

normally formed, unstable dichloro-additive compound (I). It forms transparent, rhombic, bipyramidal, plate-like crystals, m. p. 173—174°, b. p. ca. 130°/10 mm. In addition, a liquid dichloride, b. p. ca. 120—125°/10 mm., which could not be isolated in the pure condition, is also produced. Neither dichloride is affected by boiling aniline.

Preliminary experiments show that pinene hydrochloride can be readily chlorinated in chloroform or carbon tetrachloride solution until four additional atoms of hydrogen have been replaced. Colourless, crystalline products, m. p.'s 135°, 150—152°, and 130° respectively, have thus been obtained, analyses of which give results intermediate between those required for $C_{10}H_{15}Cl_3$ and $C_{10}H_{14}Cl_4$; the formation of a dichloride was not observed. H. W.

The Relative Power of Addition of Unsaturated Compounds. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1916, 58, 9 pp.; from *Chem. Zentr.*, 1919, ii, 953).—The action of pinene on different terpene hydrochlorides, particularly at elevated temperature, regularly occurs in such a manner that hydrogen chloride is withdrawn from the latter and ordinary pinene hydrochloride (bornyl chloride) is produced; this is demonstrated in the cases of dipentene dihydrochloride, sylvestrene dihydrochloride, camphene hydrochloride, and dipentene monohydrochloride. Pinene can even remove hydrogen chloride slowly from dry aniline hydrochloride or ammonium chloride. Nopinene and the bicyclic terpene, b. p. 163—165°, recently isolated from Finnish oil of turpentine and provisionally termed γ-pinene, behave similarly to ordinary pinene. In like manner, hydrogen bromide is removed by pinene from camphene hydrobromide or dipentene dihydrobromide. When heated with aniline sulphate and acetic acid, pinene gives *iso*bornyl acetate. On account of its unsaturated nature, pinene behaves in this respect as a base. Even with complex halogen additive products, such as dipentene tetrabromide, pinene effects the removal of halogen acid. This behaviour of pinene and analogous substances is probably attributable to the relatively great latent heat of these terpenes. H. W.

Preparation of Organic Camphol Esters and of Borneol from them in the Presence of Sulphoricinic Acid, which Acts as a Solvent for Camphene or Pinene Hydrochloride. ANDRÉ DUBOSC (*Caoutchouc et Guttapercha*, 1918, **15**, 9555; from *Chem. Zentr.*, 1920, i, 115).—The difficulty of preparing organic camphol esters lies, in part, in the sparing solubility of the substances to be esterified in the acids used; it is now shown that solution can be effected by the addition of sulpho-compounds, particularly of sulphoricinic acid, and that these do not take further part in the action. The separation of ester from sulphoricinic acid and from excess of the acid under esterification occurs in the usual manner. The corresponding camphor alcohols may be obtained by hydrolysis of the esters. H. W.

New Hydrocarbons of High Molecular Weight from Isoprene. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc*, 1916, **58**, 12 pp.; from *Chem. Zentr.*, 1918, ii, 954—955).—The additive capacity of caoutchouc shows that one double bond of isoprene disappears in its formation, and is utilised in uniting the condensed isoprene molecules. The molecules which are thus formed by purely chemical reaction are subsequently united to greater complexes, probably by physical and secondary chemical forces (such as residual affinities). According to the author, therefore, two processes are operative in the formation of caoutchouc, which differ from one another not only in respect of rapidity, but also of nature, namely, first, a purely chemical condensation involving certain ethylenic bonds in isoprene and leading to new carbon compounds, and, secondly, formation of greater complexes from the "simplest caoutchouc molecules" so formed which does not involve the production of carbon compounds in the ordinary sense. The latter process only takes place gradually, and is probably never complete; it constitutes the so-called polymerisation of caoutchouc. The converse process, depolymerisation, occurs when caoutchouc forms additive products and when it is dissolved, particularly in hot solvents.

The properties of caoutchouc tetrabromide show it to have a molecular weight which cannot be estimated by the ebullioscopic method. The formation of the complex molecule cannot, however, be a subsequent operation, since the additive product is itself saturated. Bromine is added at the double bonds which remain after or are formed during the polymerisation of isoprene, and in proportion as addition proceeds at the "simplest caoutchouc molecules" the powers of complex formation, present in the caoutchouc, are placed out of action; the state of division of the substance probably remains at the stage corresponding with the "simplest caoutchouc molecules." According to this view, the molecules of caoutchouc and its bromide are both large, but of different orders of magnitude. The tetrabromide is therefore actually amorphous, but has not the viscous consistency of caoutchouc, which indicates a very high molecular weight. The same may be said for most of the other additive products of rubber. In experimental confirmation of the view that the synthesis of caoutchouc takes place in two stages, it is shown that isoprene condenses with other hydrocarbons containing an ethylenic linking, such as amylene (β-methyl-Δ^{β}-butylene), pinene, camphene, and with itself, yielding compounds of very high molecular weight which are amorphous, but do not possess the physical properties of caoutchouc. Both the course of the reaction and the mode of action of the necessary catalyst ($AlCl_3$) indicate that the process is one of actual condensation which proceeds to completion. The products are still unsaturated, but add much less bromine than does caoutchouc. Two different classes of compounds are invariably formed, both of which are solid, but of which the one (*A* product) is completely insoluble in all solvents, whilst the other (*B* product) dissolves in most organic media with

the exception of alcohol. Isomerism probably depends on difference in molecular weight.

A large number of individual experiments are described in the original which do not lend themselves to abstraction. Commercial isoprene yields two different *products* with aluminium chloride; both have the composition $(C_{10}H_{18})_n$, but, as was found subsequently, the nature varies with differing proportions of isoprene and amylene. The consecutive products obtained by the step-wise condensation with aluminium chloride have the same percentage composition. Soluble and insoluble substances are alike unsaturated, and have almost identical additive powers. Pure isoprene and pure β-methyl-Δ^{β}-butylene, when separately treated with aluminium chloride, give products of a completely different type. Experiments with mixtures of the two showed that practically only the isoprene of the mixture was acted on if the proportion of amylene was small and the action was cautiously performed. The condensation products must therefore be regarded as polymerised isoprenes. They are not identical, but isomeric, with caoutchouc. Oily substances are obtained as by-products of these condensations, which are possibly synthetic hydrocarbons of the sesqui-, di-, and poly-terpene series. It is further shown that isoprene can be condensed with pinene and camphor to products similar to those formed with β-methyl-Δ^{β}-butylene; it condenses, in addition, with *iso*pinene, dipentene, and sylvestrene. H. W.

Digitalis Substances. XL. H. KILIANI (*Ber.*, 1920, **53**, [*B*], 240—250).—In a previous communication (A., 1919, i, 214), the author has described the degradation of digitogenic acid into a lactone, $C_8H_{12}O_2$, and a monobasic acid. Further examination of the former and the preparation of an *acetyl* derivative, m. p. 89—90°, lead to the adoption of the formula $C_{12}H_{18}O_3$, and this is confirmed by a study of the *magnesium* salt of the corresponding acid. It is also found that the lactone contains 10—15% of a *substance*, $C_{12}H_{18}O_3$, m. p. 76°, which is not dissolved by boiling dilute aqueous alkali, and that the lactone cannot be recovered as such from its solutions in alkali. Revision of the formula of the lactone necessitates alteration in that of the monobasic acid, which should have the composition $C_{16}H_{26}O_5$; re-examination of the product shows that it is not homogeneous, but contains ethyl hydrogen digitogenate, after removal of which, however, the acid still does not conform to the expected formula.

Digitaligenin has $[\alpha]_D$ +454° in 95% alcohol, +443° in alcohol whilst the hydro-product (A., 1919, i, 91) has $[\alpha]_D$ +42° in 95% alcohol; contrary to the previous statement, the latter yields only a monoacetyl derivative, m. p. 165°. Digitaligenin is converted by formic acid in the presence of sodium formate into a *monoformyl* derivative, leaflets, m. p. 169°; and is not hydrolysed by treatment with hot dilute alcoholic hydrochloric acid.

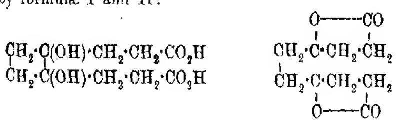
Digitoxigenin is not hydrolysed by 2% hydrochloric acid, but is converted into a *substance*, $C_{22}H_{32}O_4$, m. p. 175°; *acetyldigitoxigenin*

forms short, coarse rods, m. p. 211—212°. Cautious oxidation of digitoxigenin by chromic acid converts it into a crystalline substance, $C_{19}H_{26}O_4$, which is converted by alcoholic hydrochloric acid into toxigenone, m. p. 260°; the latter is slowly transformed by hot alcoholic sodium hydroxide solution into an amorphous sodium derivative, and hence, contrary to previous statements, appears to have lactonic character.

Sodium dixgeninate is oxidised by cold potassium permanganate solution, yielding an *acid*, $C_{17}H_{24}O_6,1\cdot5H_2O$, platelets, m. p. 218—219°, $[\alpha]_D$ $-31\cdot4°$, as potassium salt (the *calcium* salt, $C_{17}H_{12}O_6Ca,1\cdot5H_2O$ was analysed); the acid is not affected by an excess of hot sodium hydroxide solution or by cold permanganate, and only slowly by hot permanganate. On the other hand, it is very susceptible to hot hydrochloric acid, which converts it into an *acid*, needles, m. p. 120°, equivalent ca. 300. It is converted by nitric acid into an *acid*, which becomes discoloured at 235° and has m. p. 270° (decomp.); the *calcium* salt was analysed. The investigation of these acids is not yet complete. H. W.

A New Glucoside Hydrolysable by Emulsin: Scabiosin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, **170**, 486—491).—The roots of *Scabiosa succisa*, L., contain sucrose, obtainable in a crystalline form, and also a new glucoside, *scabiosin*, $[\alpha]_D$ $-106\cdot52°$, which, when hydrolysed by emulsin or by dilute sulphuric acid, gives dextrose and a yellow substance insoluble in water. W. G.

Tetrahydroanemonin. Y. ASAHINA and M. ATSUMI (*J. Pharm. Chim.*, 1920, [vii], **21**, 135—136).—Tetrahydroanemonin, $C_{10}H_{12}O_4$, when treated with sodium ethoxide in alcoholic solution, gives a *sodium* salt, $C_{10}H_{14}O_6Na_2$, very soluble in water, and no longer possessing the ketonic function of anemonin. When acidified, the sodium salt gives, not an acid, but tetrahydroanemonin, which therefore seems to be the dilactone of an unstable acid. The constitutions assigned to this acid and the tetrahydroanemonin are given by formulæ I and II:



(I.) (II.)

The sodium salt, on oxidation in neutral solution with potassium permanganate, yields the sodium salt of anemonolic acid, $CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$. W. G.

Use of Butyl Alcohol as a Solvent for Anthocyanins. OTTO ROSENHEIM (*Biochem. J.*, 1920, **14**, 73—74).—Butyl alcohol removes all the anthocyanins from their solutions in dilute acids. Comparative tests show that the monoglucosides, chrysanthemin

and oenin, are four times as soluble in butyl alcohol as in amyl alcohol; idaein is ten times as soluble. Of the rhamno-glucosides, prunicyanin is sixteen times as soluble, and violanin is twenty-five times as soluble, as in amyl alcohol. Butyl alcohol, therefore, is a suitable solvent for use in the preparation of these substances in the pure condition. The author has prepared pure specimens of oenin from grapes and pure idaein from cranberries by means of this solvent. J. F. S.

Tannins. III. Chlorogenic Acid, the Tannin-like Constituent of Coffee. KARL FREUDENBERG (*Ber.*, 1920, **53**, [*B*], 232—239).—Chlorogenic acid has been extensively investigated by Gorter (A., 1911, i, 221, and previous abstracts), who has assigned to it the annexed formula:

$$O\left\{CH[C_6H_3(OH)_2]\cdot CH\cdot \underset{\displaystyle CO_2H}{\overset{|}{C}}(OH)\cdot C(OH){<}\begin{matrix}CH_2\text{——}CH\\ CH(OH)\cdot CH_2\end{matrix}{>}CH\cdot OH\right\}_2$$

This is not easily reconciled with the production of caffeic acid from it under the influence of *Mucor* or *Penicillium* varieties. Repetition of the fission experiments, using tannase, has shown that chlorogenic acid yields caffeic and quinic acids. It has also been found that chlorogenic acid, which Gorter considered to be anhydrous, actually contains $\frac{1}{2}H_2O$; this accounts for the difference between it and the hypothetical hemichlorogenic acid. Chlorogenic acid thus appears simply as a depside of caffeic and quinic acids, and, as appears from Gorter's experiments, the carboxy-group of caffeic acid is united to a hydroxy-group of quinic acid, as indicated by the formula

$$C_6H_3(OH)_2\cdot CH{:}CH\cdot CO\cdot O\cdot C_6H_7(OH)_3\cdot CO_2H.$$

H. W.

The Action of Sodium Hypochlorite on Amides. I. J. RINKES (*Rec. trav. chim.*, 1920, **39**, 200—207).—Sodium hypochlorite acts on $\alpha\beta$-unsaturated amides in the presence of methyl alcohol to give urethanes, which, when hydrolysed with dilute sulphuric acid, yield saturated aldehydes, containing one atom less of carbon than the original amide.

Furylacrylamide, $C_4H_3O\cdot CH{:}CH\cdot CO\cdot NH_2$, under these conditions yields *furylvinylurethane*, $C_4H_3O\cdot CH{:}CH\cdot NH\cdot CO_2Me$, m. p. 102°, which on hydrolysis gives *furylacetaldehyde*, $C_4H_3O\cdot CH_2\cdot CHO$, giving a p-*nitrophenylhydrazone*, m. p. 126°, and a *semicarbazone*, m. p. 130°.

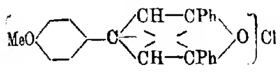
Cinnamaldehyde condenses with cyanoacetic acid to give α-cyanocinnamenylacrylic acid, which, when heated with copper powder, yields cinnamenylacrylonitrile, and this when allowed to remain in contact with fuming hydrochloric acid and ether, gives cinnamenylacrylamide. This amide, with sodium hypochlorite and methyl alcohol, yields *cinnamenylvinylurethane*,

$$CHPh{:}CH\cdot CH{:}CH\cdot NH\cdot CO_2Me,$$

m. p. 134—135°, which is hydrolysed by sulphuric acid to *β-benzylidenepropaldehyde*, $CHPh{:}CH{\cdot}CH_2{\cdot}CHO$, giving a *p-nitrophenylhydrazone*, a *semicarbazone*, m. p. 192° (decomp.), and an *oxime*, m. p. 117°. W. G.

Pyrylium Compounds. VI. Quino-pyran Derivatives. W. DILTHEY and R. TAUCHER (*Ber.*, 1920, **53**, [*B*], 252—260).—In extension of the work of Dilthey (A., 1919, i, 413), pyrylium salts having a methoxy- or hydroxy-group in the *para*-position in the phenyl group in position "4" have now been prepared which are found to be closely analogous to the corresponding salts in which the α-phenyl group is similarly substituted.

Anisylidenediacetophenone, $OMe{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}CO{\cdot}C_6H_5)_2$, colourless, coarse crystals, m. p. 105°, is prepared by the condensation of anisaldehyde and acetophenone with sodium hydroxide in boiling aqueous alcoholic solution; a second *modification*, long, shining crystals, m. p. 93°, is also described, which passes into the former when crystallised from benzene. The *disemicarbazone* forms colourless crystals, m. p. 246—247°. Anisylidenediacetophenone (or a mixture of anisylideneacetophenone and acetophenone) is converted by hydrated ferric chloride in acetic anhydride solution into the *iron* salt of 2:6-diphenyl-4-*p*-anisylpyrylium chloride (annexed formula), small, yellow needles, m. p. 226°, which is transformed by sodium acetate



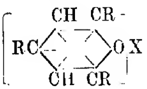
in dilute aqueous solution into *α-hydroxy-ε-keto-αε-diphenyl-*γ-p-*anisyl-Δ^{αγ}-pentadiene*, $OH{\cdot}CPh{:}CH{\cdot}C(C_6H_4{\cdot}OMe){:}CH{\cdot}COPh$, slender needles, m. p. 122° (*disemicarbazone*, colourless crystals, m. p. 218°; *picrate*, reddish-brown needles, m. p. 244°; *acid hydrochloride*, yellow, crystalline precipitate, which decomposes at about 140°). Demethylation of the *pseudo*-base with concentrated hydrochloric acid at 160—170° gives 2:6-*diphenyl-4-*p-*hydroxyphenylpyrylium hydrochloride*, steel-blue, shining needles, m. p. 320°, after slowly changing from 235° (an *acid chloride*, $C_{23}H_{17}O_2Cl,0{\cdot}5HCl$, yellow crystals, is also described); demethylation with hydrobromic acid gives the corresponding *bromide*, brownish-red crystals, m. p. above 320°, which appears to exhibit little tendency towards further combination with the halogen acid. The chloride is converted by water and a slight excess of sodium acetate into 2:6-diphenyl-4-quinopyran, $O{<}{\substack{CPh{:}CH\\CPh{:}CH}}{>}C{:}C_6H_4{:}O$, dark red crystals with a bronze glance, m. p. 262—264°; the anhydro-base is almost instantaneously decolorised by semicarbazide, but does not yield a semicarbazone. Addition of water to the anhydro-base occurs less readily than with the α-isomeride, and is best effected by cautious addition of water to the alcoholic solution, whereby the *carbinol* base, $O{<}{\substack{CPh{:}CH\\CPh{:}CH}}{>}C{<}{\substack{OH\\C_6H_4{\cdot}OH}}$, is precipitated in pale red crystals. It is much less stable than the corresponding α-derivative, and

readily loses water when heated, and re-forms the pseudo-base. It is more readily isolated as its *monoacetyl* derivative, pale yellow, silky needles, m. p. 122—123°.

Prolonged action of pyridine on the demethylated chloride leads to the formation of two *substances*, $C_{23}H_{20}O_4$, needles, m. p. 166°, and $C_{23}H_{20}O_6$, colourless crystals, m. p. 239—240°, respectively. These compounds do not exhibit any relationship to the red anhydro-base, and are probably formed by fission of the ring.

[*Addendum to Part IV*.—W. DILTHEY.]—The *disemicarbazone* of α-hydroxy-ε-keto-γε-diphenyl-α-p-hydroxyphenyl-$\Delta^{\alpha\gamma}$-pentadiene forms colourless, transparent prisms, m. p. 191—192°. The acid picrate of 2:6-diphenyl-4-*p*-anisylpyrylium, m. p. 237—238° (A., 1919, i, 413) is now found to have a normal constitution. H. W.

Pyrylium Compounds. VII. Carbonium or Oxonium? WALTHER DILTHEY (*Ber.*, 1920, **53**, [*B*], 261—265).—The author is led to reject the carbonium formula for pyrylium compounds, since several basic carbon atoms must be taken into consideration, and thus there is no possibility of a uniform conception. For a similar reason, the oxonium formula is rejected. Regarding the basic properties of oxygen as proved, there would be in the pyrylium salts three carbon atoms and two oxygen atoms to which negative radicles might be attached, whilst it is also possible that the para-carbon atom of the phenyl residue can function in the formation of salts. In proportion as the number of basic atoms in the molecule increases, it becomes more certain that no single one of them is united to the negative group, and more probable that the latter is attached to the molecule as a whole. A somewhat similar idea has been advanced by Kauffmann (this vol., i, 50), who, however, regards the cationic partial valencies as associated with definite atoms. It appears simpler to the author to regard the complex as a whole rather than the individual atoms as carriers of the electron. Adopting these ideas, the annexed formula is proposed for the pyrylium salts, which represents the negative group as freely mobile in the "second" zone and attached to no particular atom, but to the total complex. The fourth carbon valencies are disposed in such a manner as to indicate that one of them resembles the carbon atom of triphenylmethyl, and to express the possibility of the return of the hydroxyl group in the formation of pseudo-bases to either the α- or the γ-carbon atom. When this has occurred, the remaining valencies arrange themselves to ordinary double bonds; it is also shown that the β-carbon atoms cannot combine with the hydroxyl. Since this conception can readily be expanded to triphenylmethyl and to the nitrogen atoms of azines, oxazines, and thiazines, a uniform conception of a large class of dye-salts is secured.



H. W.

Syntheses of Methylenecoumarins. L. CLAISEN (*Ber.*, 1920, **53**, [*B*], 322—325).—In a recent communication (A., 1919, i, 340), Adams and Rindfuss have described the action of bromine on acetylated *o*-allylphenols and the elimination of the bromine from the product by boiling alcoholic potassium hydroxide, whereby they obtain substances which they consider to be methylenecoumarans of the type $C_6H_4<{CH_2 \atop O}>C{:}CH_2$. The author points out that he has used this process previously (A., 1913, i, 1175; 1919, i, 266), and that it yields coumarones of the type $C_6H_4<{CH \atop O}>CMe$. Whilst agreeing with Adams and Rindfuss that the compound $C_6H_4<{CH_2 \atop O}>CH{\cdot}CH_2Br$ is formed as an intermediate stage, he does not consider that the further elimination of hydrogen bromide must of necessity cause the final production of a substance with the double bond in the side-chain, since, under the experimental conditions, one of the two bonds would almost certainly pass to the nucleus. Further, the observation of Adams and Rindfuss that their "methylenecoumaran" yields a monobromo-derivative from which bromine cannot be removed by alcoholic potassium hydroxide or silver nitrate, is most readily explained on the assumption that it is a methylcoumaran brominated in the nucleus.

H. W.

4′-Methoxy-1′-naphthyl-2-chromone. S. RUHEMANN and S. I. LEVY (*Ber.*, 1920, **53**, [*B*], 265—274).—4-Methoxy-1-naphthaldehyde, b. p. 200—202°/10 mm., is converted by ethyl acetate and metallic sodium into *ethyl β-4-methoxy-1-naphthylacrylate*, $OMe{\cdot}C_{10}H_6{\cdot}CH{:}CH{\cdot}CO_2Et$, yellow prisms, m. p. 59°, which is readily hydrolysed to the corresponding acid, m. p. 215° (compare Rousset, A., 1899, i, 296; Windaus and Bernthsen-Buchner, A., 1917, i, 670). The latter is reduced by sodium amalgam to β-4-methoxynaphthylpropionic acid, colourless needles, m. p. 163—164° (Windaus and Bernthsen-Buchner, *loc. cit.*, give 165—166°), the *silver* salt and *ethyl* ester, colourless oil, b. p. 206—207°/10 mm., of which are described. Attempts to convert the acid into a hydrindone by means of phosphorus pentachloride and aluminium chloride were unsuccessful, the product being an oil, which did not crystallise and could not be distilled without decomposition.

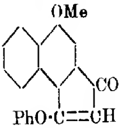
Ethyl αβ-dibromo-β-4-methoxy-1-naphthylpropionate,

$$OMe{\cdot}C_{10}H_6{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2Et,$$

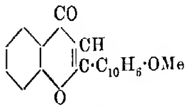
colourless needles, m. p. 108—109° (decomp.), is obtained in quantitative yield from the unsaturated ester and bromine in carbon disulphide solution. It is a somewhat unstable substance, which readily decomposes when gently warmed; it is converted by alcoholic potassium hydroxide solution into *4-methoxy-1-naphthylpropiolic acid*, yellow needles, m. p. 159° (decomp.), from which

4-*methoxy*-1-*naphthyl methyl ketone*, colourless prisms, m. p. 72—73°, is prepared by prolonged treatment with boiling water. Methoxynaphthylpropiolic acid cannot be esterified in the usual manner; thus, treatment with boiling 2—3% alcoholic hydrogen chloride converts it into *ethyl β-chloro-4-methoxy-1-naphthylacrylate*, $OMe\cdot C_{10}H_6\cdot CCl\colon CH\cdot CO_2Et$, yellow, viscous oil, b. p. 230—240°/15 mm. (partial decomp.). *Methyl 4-methoxy-1-naphthylpropiolate*, colourless needles, m. p. 97°, is prepared from the acid, methyl sulphate, and potassium hydroxide, whilst the *ethyl* ester, yellow prisms, m. p. 81—82°, is similarly obtained, but in very poor yield, with the aid of ethyl iodide.

Ethyl β-phenoxy-β-4-methoxy-1-naphthylacrylate is prepared as a viscous, red oil, which did not show any tendency to crystallise, and which was not further purified by the action of sodium phenoxide on ethyl β-chloro-β-4-methoxy-1-naphthylacrylate; it was hydrolysed by methyl-alcoholic potassium hydroxide to a mixture of the corresponding *acid*, brown prisms, m. p. 180—181° (decomp.), and the *phenyl ether* of 3-*hydroxy*-8-*methoxy*-*αβ*-*naphthind*-1-*one* (I), colourless prisms, m. p. 186—187°. Successive treatment of β-phenoxy-β-4-methoxy-1-naphthylacrylic acid with phosphorus pentachloride and aluminium chloride yields 4′-*methoxy*-1′-*naphthyl*-2-*chromone* (II), pale yellow needles, m. p. 177—178°. H. W.



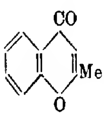
(I.)



(II.)

Formation of Chromones. S. RUHEMANN (*Ber.*, 1920, **53**, [*B*], 285—287).—The methods available for the synthesis of chromones (Ruhemann, T., 1900, **77**, 1184; 1901, **79**, 470, 918, 1185; 1902, **81**, 419; Simonis and Rennert, A., 1914, i, 980) suffer under the disadvantage that the yields are very small. The author has therefore endeavoured to synthesise these substances from ethyl β-chlorocrotonate, using a procedure which, in the aromatic series, readily yielded the flavones; although preparation can be effected in this manner, the yields are unsatisfactory.

2-Methylchromone (annexed formula), colourless needles, m. p. 72—73°, is obtained by the successive action of phosphorus pentachloride and aluminium chloride on β-phenoxycrotonic acid. Similarly, β-p-*tolyloxycrotonic acid*, colourless needles, which gradually decompose when heated, softening at 145° and becoming completely molten at about 159—160° (*ethyl* ester, colourless oil, b. p. 152—153°/14 mm.), is transformed into 2:6-*dimethylchromone*, colourless prisms, m. p. 103—104°; the latter, like other chromones (Ruhemann, T., 1902,



81, 419), yields a *platinichloride*, $(C_{11}H_{10}O_2)_2,H_2PtCl_6$, orange prisms, which darken when heated and have m. p. 185° (decomp.).

H. W.

The Parent Substance of Adrenaline. KARL W. ROSENMUND and H. DORNSAFT (*Ber.*, 1920, **53**, [*B*], 317—318. Compare this vol., i, 56).—In reply to the criticism of Knoop (this vol., i, 161), the authors point out (i) that adrenaline is produced in such small quantity in the organism that it is probable that the main processes of degradation of amino-acids are not concerned with its formation, and (ii) that the sequence of changes of amino-acids which they have postulated is not hypothetical, but is based on changes which have been established experimentally for micro-organisms.

H. W.

The Identity of Aribine with Harman. ERNST SPÄTH (*Monatsh.*, 1919, **40**, 351—359).—The fact that aribine can be sublimed without decomposition is difficult to reconcile with the molecular weight required by Rieth's formula, $C_{23}H_{20}N_4$ (*Annalen*, 1861, **120**, 247). A comparison of the alkaloid with harman, $C_{12}H_{10}N_2$ (Fischer, A., 1901, i, 405), revealed the complete identity of the bases (m. p. 237—238° in a vacuum), of their hydrochlorides (each showing intense blue fluorescence in acid solution), of their aurichlorides (darkening in a vacuum at 207° and melting at 211—213° [decomp.]), of their platinichlorides (straw-yellow needles, which turn brown in a vacuum at 255—260°, and are not melted at 280°), and of their picrates (yellow crystals, which become brown in a vacuum at 215°, dark brown at 240°, and black at 250—255°).

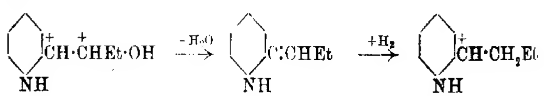
J. K.

Some New Compounds of Caffeine and Theobromine, Soluble in Water. J. ABELIN (*Apoth. Zeit.*, **34**, 316; from *Chem. Zentr.*, 1919, iii, 957).—The alkali and alkaline-earth salts of aromatic carboxylic acids and of all ω-methylsulphonic acids of carbo- and hetero-cyclic amines yield complex compounds with caffeine and theobromine which are freely soluble in water and, in part, are of therapeutic value. Since aqueous solutions of *o*-acetoxybenzoic acid are readily decomposed, with elimination of acetic acid when slightly warmed, the preparation of *calcium caffeine-o-acetoxybenzoate* is effected by suspending calcium *o*-acetoxybenzoate (100 grams) in anhydrous alcohol or acetone (500 c.c.), and, with continuous stirring, adding a solution of caffeine (55 grams) in chloroform; the solvent is subsequently allowed to evaporate at a low temperature. The purity of the product is tested by treating its aqueous solution with ferric chloride, which should yield a coffee-brown precipitate, but not a violet coloration (absence of salicylic acid). *Calcium theophylline-o-acetoxybenzoate* is similarly prepared from solutions of theophylline in pyridine or benzyl alcohol. The caffeine and theophylline *compounds* of the ω-methyl-

sulphonates of the amines are prepared by mixing solutions of equimolecular quantities of the components in water and evaporating the solutions on the water-bath at a low temperature, or, if the amine salt is insufficiently stable to withstand this treatment, a solution of caffeine in chloroform is added to a suspension of the sodium salts of the ω-methylsulphonic acids of *p*-phenetidine (neraltine), of 4-aminoantipyrine (melabrin), of aniline, *p*-toluidine, or naphthylamine in alcohol, acetone, or chloroform, and the solvent is removed with continuous stirring at a gentle temperature.

H. W.

The Ability of Plants to Form Optical Antipodes. KURT HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [*B*], 119—129).—The normal products of animal metabolism occur in optically active forms and never in their possible antipodes; an apparent exception to this rule is found in the production of optically inactive lactic acid by the fermentation of dextrose, but in this case it has been established that methylglyoxal is an intermediate product, from which, by an intramolecular Cannizzaro reaction, the lactic acid is finally formed, that is, the final stage is not an enzymic process. In the case of the plant organism, on the other hand, optical antipodes are not infrequently produced simultaneously; examples of this are coniine and methylconiine in *Conium maculatum*, pelletierine, *iso*pelletierine and methyl*iso*pelletierine, atropine, laudanine, scopoline, paricine, cryptopine, arabine, cevadine, delphinine, and delphinoidine. The production of optically inactive bases which contain at least one asymmetric carbon may be ascribed to one of the following causes: (i) racemisation may have occurred during the treatment of the plant with extracting solvents, (ii) racemisation of a primarily formed optically active alkaloid may have occurred within the plant during its life, and (iii) formation of the alkaloid may be brought about by "symmetrical" processes, either by symmetrical enzymes or by total or partial processes in which enzymes do not play a part. Thus, coniine may possibly be formed in the following manner:



which would be analogous to the production of *dl*-lactic acid from dextrose, with intermediate formation of methylglyoxal. The possibility indicated in (i) may be exemplified by atropine, since *l*-hyoscyamine is readily racemised by dilute alkali at the ordinary temperature and by preservation of its alcoholic solution, whilst protracted treatment with potassium carbonate solution is used in extracting the alkaloid from *Atropa belladonna*. Pelletierine and the allied substances have been shown to be readily racemised, but not under conditions such as are observed in their extraction, whilst,

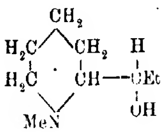
also, no activity is observed in the fresh extracts. *d*-Coniine and *d*-methylconiine are racemised with such difficulty that it is impossible to assume that racemisation occurs in the process of extraction or within the living plant. The case of scopoline is somewhat different, and it appears impossible to attribute the optical inactivity of the natural product to any of the three causes above-mentioned, since King (T., 1919, **115**, 476, 974) has shown that the active base is by no means readily racemised, and an explanation on the lines of that given for *dl*-lactic acid is out of the question. There would thus appear to be an example of a fundamentally different mode of action in the animal and the plant organism.

[In part with (FRL.) H. KAULLA.]—Coniine is not racemised when heated with concentrated hydrochloric acid during 104 hours at about 200° (compare Hess and Eichel, A., 1918, i, 34). Similarly, *d*-methylconiine is unchanged by similar treatment during 120 hours, by the action of ethyl-alcoholic sodium ethoxide solution during 12 hours at 200°, or of aqueous ethyl-alcoholic sodium solution under the same conditions, or by boiling alcoholic potassium hydroxide solution during 45 hours. H. W.

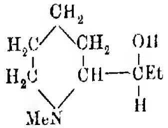
The Asymmetric, Tervalent Nitrogen Atom. III. Methyldihydro*iso*pelletierine and *dl*-Methylconhydrine [Methyldihydroconhydrinone]. KURT HESS (*Ber.*, 1920, **53**, [*B*], 129—139).—In previous communications (A., 1919, i, 345; this vol., i, 86) it has been shown that methyl*iso*pelletierine and *dl*-methylconhydrinone are structurally identical, racemic compounds, the isomerism of which can only be explained by the assumption of a second asymmetric centre in addition to the asymmetric carbon atom, which can only be the tervalent nitrogen atom. Since each compound is oxidised to piperidine-2-carboxylic acid and reduced to *dl*-methylconiine, it appeared that the stereoisomerism was in some manner conditioned by the presence of the carbonyl group. It is now found, however, that the four amino-alcohols obtained by reduction of methyl*iso*pelletierine and *dl*-methylconhydrinone are all different, so that the isomerism of the parent substances persists in the corresponding alcohols. The carbonyl group of the ketones cannot therefore have the importance which was previously attributed to it, and the cause of the isomerism is to be sought in the arrangement of the groups around the nitrogen atom. If, however, the oxygen atom is entirely removed, the isomerism disappears. It may be further noted that the methiodides of the hydramines of both series are different, and afford a rather unusual example of asymmetric arrangement in a compound of the type N(AABC)X; a similar instance has been observed by Freund and Kessler (A., 1919, i, 283) in the quinoline series.

Methyl*iso*pelletierine is readily reduced by sodium amalgam and water at the ordinary temperature to a mixture of *a-methyldihydro*iso*pelletierine*, b. p. 101—106°/15 mm., and slightly impure

β-methyldihydroisopelletierine, b. p. 115—120°/15 mm. (annexed formulæ), which are separated by fractional distillation. The α-base does not yield crystalline salts with the halogen acids or with chloroplatinic acid, but gives a crystalline methiodide,



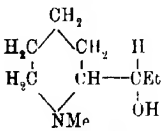
α-Base.



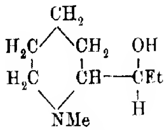
β-Base.

m. p. 176°, an oily *picrate*, and an oily m-*nitrobenzoyl* derivative, b. p. ca. 220°/17 mm. The β-base gives a *methiodide*, cubes, m. p. 176—177°, a *picrate*, prisms, m. p. 123—124°, and an oily m-*nitrobenzoyl* derivative, which could not be distilled without almost complete decomposition. Reduction of either base by phosphorus and hydriodic acid at 125—135° gave *dl*-methylconiine, identified as the platinichloride and aurichloride.

α-dl-*Methylconhydrine*, b. p. 97—99°/16 mm., and β-dl-*methylconhydrine*, b. p. 91—101°/15 mm. (annexed formulæ), are obtained by the action of formaldehyde and formic acid on the corresponding hydramines. The α-base gives a *methiodide*, prisms, m. p. 178—179°, a *picrate* (+0·5EtOH), rods,



α-Base.



β-Base.

m. p. 79—80°, and an oily m-*nitrobenzoyl* derivative. The *methiodide* of the β-base crystallises in prisms, m. p. 174°, the *picrate* forms irregular plates and cubes, m. p. 133—134°, and the m-*nitrobenzoyl* derivative is an oil. Reduction of either base by hydriodic acid and red phosphorus yields *dl*-methylconiine.

Isomerism of the amino-alcohols is not so sharply marked as that of the ketones, since in the former case the m. p.'s of the salts are nearly identical, whilst in the latter case they differ by 30—40°; the individuality of the salt is, however, readily demonstrated by the mixed melting-point method. H. W.

The Asymmetric, Tervalent Nitrogen Atom. IV. Non-existence of Ladenburg's *iso*Coniine. Kurt Hess and Wilhelm Weltzien (*Ber.*, 1920, **53**, [*B*], 139—149).—Some years ago Ladenburg (A., 1906, i, 692, and previous abstracts) described the preparation of *iso*coniine, and explained its isomerism with coniine by the hypothesis of an asymmetric, tervalent nitrogen atom. On theoretical grounds, the authors have been led to doubt the existence of this instance, since the salts of coniine and *iso*coniine have identical melting points, which is unusual in a case of this kind, whilst, secondly, *dl*-methylconiine (preceding abstract) is incapable

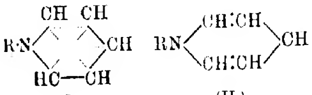
of existence in the corresponding isomeric forms, and the same is therefore probably true for coniine itself, and, thirdly, *l*-coniine has been synthesised by Löffler (A., 1909, i, 180) and found to be identical with the natural substance. They have therefore repeated Ladenburg's work, and obtained results which are practically identical with his. The possibility that *iso*coniine as prepared in this maner is contaminated with an impurity which affects the specific rotation, but is eliminated in the purification of the salts, has been examined by adopting a different mode of synthesis, which is found to yield a material identical in all respects with natural *d*-coniine. The higher optical activity of Ladenburg's synthetic coniine preparation is therefore to be attributed to the presence of impurities, and *iso*coniine is to be deleted from the literature.

Ladenburg's synthesis has been slightly modified. Methyl-α-picolylalkine is reduced by phosphorus and hydriodic acid, but as the product is found to contain about 65% of 2-allylpyridine, the conversion to the propyl derivative is completed by means of hydrogen in the presence of platinum. The *dl*-coniine is prepared by reduction of 2-propylpyridine by sodium and alcohol, and is resolved by *d*-tartaric acid. The hydrogen tartrate and platinichlorides of the synthetic and natural bases appeared identical in all respects, but the synthetic base had $[\alpha]_D + 19{\cdot}01^\circ$, whereas the natural product had only $[\alpha]_D + 15{\cdot}21^\circ$.

The preparation of *dl*-coniine from methyl α-picolylalkine has been effected in a somewhat different manner, in that the substance is first converted into the piperidine derivative by hydrogen in the presence of platinum, and the hydroxy-group is subsequently reduced by treatment with phosphorus and hydriodic acid, followed by zinc and sulphuric acid; in this manner, the formation of an allyl derivative is avoided. The racemic base is resolved by *d*-tartaric acid; the specific rotation of the hydrogen tartrate is $+20{\cdot}06^\circ$ in alcoholic solution, whilst the base obtained from it has $[\alpha]_D^{17} + 14{\cdot}96^\circ$, which agrees well with the specific rotation of the natural product. H. W.

A Radicle with Quadrivalent Nitrogen. Bruno Emmert (*Ber.*, 1920, **53**, [*B*], 370—377).—Dimethyl- or diethyl-tetrahydro-dipyridyl, $R{\cdot}N<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CH{\cdot}CH<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>N{\cdot}R$ (Hofmann, A., 1881, 921; Emmert, A., 1909, i, 602; 1917, i, 221; 1919, i, 455), is soluble in alcohol, yielding a yellowish-brown solution, which, slowly at the ordinary temperature, but more rapidly when warmed, becomes deep blue; the blue coloration disappears immediately when the solution is shaken with air, but slowly reappears, and can be again removed until a molecule of oxygen has been absorbed for each molecule of substance. The phenomena are thus analogous with those observed by Schmidlin (A., 1908, i, 623) in the case of triphenylmethyl. In the present instance, there is the possibility

of the formation of two radicles (annexed formulæ, I and II) containing, respectively, a quadrivalent nitrogen or a tervalent carbon atom, which on oxidation should yield a pyridinium hydroxide or a peroxide; actually, the formation of methylpyridinium hydroxide from dimethyltetrahydrodipyridyl (identified as the chloride and platinichloride) is established. In the case of benzyltetrahydrodipyridyl, the blue coloration of the alcoholic solution is only developed on warming. Solutions in ether are yellow, and do not become blue. Solutions in chloroform are intermediate in their properties between those in ether and alcohol; the yellow solution, when preserved with exclusion of air, slowly becomes pale green to bluish-green, which may be regarded as a mixture of the yellow and blue colorations. The following experiments show that the blue solutions actually contain the radicle (I); the alcoholic solutions are instantaneously decolorised by iodine and yield *N*-alkylpyridinium iodides, as is shown by the isolation of these substances and by the estimation of ionisable iodine in the crude products. Addition of iodine to the yellow, ethereal solutions causes partial resinification; allylpyridinium iodides are also formed in small amount, together with larger quantities of yellow, amorphous powders, which could not be further purified, but which are shown to contain an atom of iodine for each pyridine nucleus. A mixture of alkylpyridinium iodide and the yellow, amorphous iodo-compound is formed from the chloroform solution.



(I.) (II.)

In the case of triphenylmethyl, the degree of dissociation, and consequently the intensity of colour of the solution, diminishes with decreasing temperature. The blue, alcoholic solutions of the dialkyltetrahydrodipyridyls become violet-red at $-80°$, whilst that of the dibenzyl derivative changes to brown, the colour in each case being restored when the solution is warmed; the reason of the non-disappearance of the colour has not been elucidated.

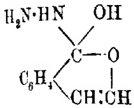
The tendency of the dialkyltetrahydrodipyridyls to dissociate into radicles is ascribed to the weakening of the valency uniting the γ-carbon atoms by the demands of the numerous double bonds, and cannot be ascribed to steric hindrance, which has been so frequently advanced as a theory in the triphenylmethyl series. H. W.

The Action of Ethyl Chloroformate on Pyridine and Quinoline. Thomas Hopkins (T., 1920, **117**, 278—282).

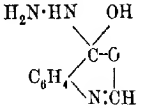
Crystallographic Properties of a Compound $C_{11}H_9O_2N$. A. Johnsen (*Centr. Min.*, 1919, 33—34).—The compound, which possibly has the structure $CHPh{:}C{<}{\begin{matrix}CO-CO\\ NH\cdot CH_2\end{matrix}}$, melts at $138{\cdot}5 \pm 0{\cdot}5°$ (decomp.), and crystallises from benzene in short columns with indistinct end faces; $a:b:c = 1{\cdot}335:1:0{\cdot}57$;

$\beta=114°18\frac{1}{2}'$. D^{16} 1·345. Cleavages were observed parallel to the faces {100} and {101}. The optic axial angle is large, and n_D 1·756. E. H. R.

Constitution of Acylanthranilic Anhydrides. G. Schroeter (*Ber.*, 1920, **53**, [*B*], 230—232).—In a recent communication (this vol., i, 181), Heller and Lauth have described the preparation of hydrazino-derivatives of simple and complex acylanthranyls, to which they have attributed the general structure $\begin{matrix}CO-\\ |\\ C_6H_4\end{matrix}\!\!>N{\cdot}COR$ instead of $C_6H_4<\begin{matrix}CO{\cdot}O\\ N{=}C{\cdot}R\end{matrix}$. The author, however, regards the formation of the hydrazine additive products as additional evidence in favour of the lactonic formulæ; he points out, for example, that the anhydride of formylanthranilic acid may be regarded as *iso*coumarin, in which a CH group is replaced by nitrogen, and that, therefore, their hydrazino-compounds may be similarly formulated (annexed formulæ, I and II).



(I.)



(II.)

The lactone formula further explains why acylanthranilic acids which contain the group ·NH·CO· readily form unimolecular anhydrides, owing to preliminary change into the desmotropic form ·N:C(OH)·, whereas those in which this desmotropic change is structurally impossible give bimolecular anhydrides. H. W.

Products of the Action of Oxalyl Chloride on Acid Anilides. R. Stollé and M. Luther (*Ber.*, 1920, **53**, [*B*], 314—317).—When acetanilide is heated with rather more than a molecular proportion of oxalyl chloride in carbon disulphide solution, it yields a *compound*, $C_{10}H_7O_3N$, m. p. 143° (not quite definite), which, mainly by reason of the readiness with which it is decomposed by water into acetic and oxanilic acids, is regarded as 4:5-diketo-3-phenyl-2-methylenetetrahydro-oxazole, $O<\begin{matrix}C(:CH_2)\\ CO{-}CO\end{matrix}>NPh$. When warmed with alcohol, it gives *4:5-diketo-2-ethoxy-3-phenyl-2-methyltetrahydro-oxazole*, colourless needles, m. p. 98°. Under similar conditions, diethylacetanilide and oxalyl chloride (1:1) give *4:5-diketo-3-phenyl-2-diethylmethylenetetrahydro-oxazole*, m. p. 69°.

The compounds obtained by Figée (A., 1915, i, 869) from molar quantities of oxalyl chloride and propionanilide or phenylacetanilide are to be regarded as 4:5-diketo-3-phenyl-2-ethylidenetetrahydro-oxazole and 4:5-diketo-3-phenyl-2-benzylidenetetrahydro-oxazole. H. W.

Preparation of Octanitrodiphenylethylenediamine. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 300082; from *Chem. Zentr.*, 1920, ii, 188).—*Octanitrodiphenylethylenediamine*,

$C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_2 \cdot CH_2 \cdot N(NO_2) \cdot C_6H_2(NO_2)_3$, is prepared by the action of concentrated nitric acid on 2:4:2′:4′-tetranitrodiphenylethylenediamine or 2:4:6:2′:4′:6′-hexanitrodiphenylethylenediamine; it crystallises from concentrated nitric acid in colourless, rhombic prisms, m. p. 213° (violent decomp.), and is almost insoluble in the usual organic media. It is an extremely sensitive explosive. H. W.

Absorptive Power of Uric Acid towards Dyes. ALBE BENOIT (*Compt. rend. soc. biol.*, 1919, **82**, 1051—1052; from *Chem. Zentr.*, 1920, i. 168).—Uric acid has the power of adsorbing precipitated colloids from their solutions. If methylene-blue is administered to a subject who separates uric acid freely, the sediment is coloured blue. If a trace of dye is added to a hot saturated solution of uric acid, coloured crystals of the latter are deposited from the cold solution. When a cold saturated solution of a normal urate is treated with a small quantity of a soluble dye and then acidified with a trace of hydrochloric acid, the precipitated uric acid adsorbs the dye, and can even cause complete decolorisation of the solution. H. W.

State of Uric Acid in Solution. ALBE BENOIT (*Compt. rend. soc. biol.*, 1919, **82**, 1052—1053; from *Chem. Zentr.*, 1920, i. 168). —Uric acid may be present in solution in two physically different conditions, in one of which it is stable, flocculent, and crystalline, and cannot adsorb dyes, whilst in the other it is metastable; it is found in the latter condition in supersaturated solution in urine. Uric acid is therefore probably more soluble in colloidal solutions than in the corresponding quantity of distilled water at the same temperature. H. W.

Action of *N*-Phenylhydroxylamine on Aromatic Nitro-compounds. JAKOB MEISENHEIMER (*Ber.*, 1920, **53** [*B*], 358—369).—The action of hydroxylamine on *m*-di- and tri-nitro-compounds leads to the substitution of hydrogen atoms attached to the nucleus by amino-groups, whereas with *o*- and *p*-dinitroaryls, reduction to the corresponding dihydro-derivatives occurs (Meisenheimer and Patzig, A., 1906, i, 642, 652). It is now shown that the reaction with phenylhydroxylamine follows a similar course in each case.

[With IVAN SMOLNIKOV.]—When *m*-dinitrobenzene and phenylhydroxylamine react in methyl-alcoholic solution in the presence of potassium hydroxide, a mixture of azoxybenzene, α-3-*nitro*-1-*azoxybenzene*, yellow needles, m. p. 120—121°, and β-3-*nitro*-1-*azoxybenzene*, pale yellow needles, m. p. 86—88°, is obtained. The latter substances are reduced by ammonium sulphide to 3-*nitro*-1-*hydrazobenzene*, yellow crystals, m. p. 84—85°, which is oxidised by mercuric oxide to 3-nitro-1-azobenzene, m. p. 95—96° (compare

Bamberger and Hübner, A., 1904, i, 117). The course of the condensation is indicated by the scheme:

$$NO_2{\cdot}C_6H_4{\cdot}NO_2 + NHPh{\cdot}OH \longrightarrow \begin{array}{c} NO_2{\cdot}C_6H_4{\cdot}N{:}O \\ \diagup\diagdown \\ NaO \quad NPh{\cdot}OH \end{array} \longrightarrow$$

$$NO_2{\cdot}C_6H_4{\cdot}N_2O{\cdot}Ph.$$

A similar mixture of azoxy-compounds is obtained from 1:3:5-trinitrobenzene, but in this instance only the more sparingly soluble 3:5-*dinitro*-1-*azoxybenzene*, practically colourless crystals, m. p. 170—171°, was isolated.

2:4-Dinitrotoluene yields with azoxybenzene. α-*benzeneazoxy*-2-*nitro*-p-*toluene*, yellow crystals, m. p. 123—124°, β-*benzeneazoxy*-2-*nitro*-p-*toluene*, m. p. 119—120°, and a substance, m. p. 160°, which is very probably 2:2′-dinitro-4:4′-azoxytoluene. Reduction of the benzeneazoxynitrotoluene yields the corresponding *hydrazobenzene*, which, without being isolated, was oxidised to *benzeneazo*-2-*nitro*-p-*toluene*, orange-red needles, m. p. 103—104°, the constitution of which is established by its synthesis from nitrosobenzene and 3-nitro-*p*-toluidine.

The nitro-group appears capable of adding hydroxylamine in the manner described above only if both the ortho-positions with respect to it are free. Thus 2:6-dinitrotoluene is converted into 2:2′-dinitro-6:6′-azoxytoluene, nearly colourless crystals, m. p. 189—190° (Brand and Zoller, A., 1907, i, 755).

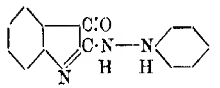
The additive power of nitro-groups in the *m*-, di-, and tri-nitro-compounds is greatly influenced by the presence of other substituents; preliminary experiments show that 2:4:6-trinitrotoluene and 2:4:6-trinitrophenetole react in a quite different manner (which has not been further examined), whilst 2:4:6-trinitro-*m*-xylene remains unaffected.

When 1:3:5-trinitrobenzene and phenylhydroxylamine are dissolved in alcohol, a crystalline *substance* is slowly deposited (pale yellow leaflets or needles, m. p. 123—124°), which is formed from 1:3:5-trinitrobenzene (2 molecules) and azoxybenzene (1 molecule), the latter being obviously formed by the auto-decomposition of phenylhydroxylamine. *m*-Dinitrobenzene behaves similarly, yielding m-*dinitrobenzeneazoxybenzene*, $C_{18}H_{14}O_5N_4$, yellow plates, m. p. 52—54°. Azoxybenzene was also found to give additive *products* with 1:3:5-trinitrobenzene, with 2:4:6-trinitrotoluene (yellow leaflets, m. p. 64—66°), and with *m*-dinitrobenzene, but not with 2:4:6-trinitrophenetole or 2:4-dinitrotoluene. Azobenzene was less reactive, but yielded an additive compound with trinitrobenzene (compare Hofmann and Kirmreuther, A., 1910, i, 548), but not with 2:4:6-trinitrotoluene, 2:4:6-trinitrophenetole, *m*-dinitrobenzene, or 2:4-dinitrotoluene. H. W.

Azo-derivatives of Indoxyl. J. Martinet and O. Dornier (*Compt. rend.*, 1920, **170**, 592—594).—Azo-derivatives of indoxyl

may readily be prepared by adding to a mixture of ice and indoxyl neutralised with sulphuric acid, the requisite amount of a diazo-compound. In this way the authors have prepared: o-*Tolueneazoindoxyl*, m. p. 249° (decomp.). m-*Tolueneazoindoxyl*, m. p. 232° (decomp.). p-*Tolueneazoindoxyl*, m. p. 256° (decomp.). m-4-*Xyleneazoindoxyl*, m. p. 244° (decomp.). *ψ-Cumeneazoindoxyl*, m. p. 245° (decomp.). *α-Naphthaleneazoindoxyl*, m. p. 202° (decomp.). *β-Naphthaleneazoindoxyl*, m. p. 220° (decomp.).

All the m. p.'s given are approximate owing to decomposition.



Benzeneazoindoxyl, when reduced in alkaline solution by sodium hyposulphite, gives aniline, ammonia, and indirubin.

The authors discuss the structure of these azo-compounds, and suggest as a possible constitution the formula annexed as an alternative to that supported by Baeyer (compare A., 1884, 74) and Heumann (compare *Ber.*, 1893, **26**, 226) or the one supported by Heller (compare A., 1907, i, 442). W. G.

Diazo-compounds. Thermochemical Investigations. W. Swientoslawski (*Ann. Soc. d'Encour. Sci. Expt.*, 1917, Suppl. No. 7. Reprint 15 pp.).—In part a very brief résumé of work already published (compare A., 1909, ii, 547, 864; 1910, ii, 588, 691; 1911, ii, 188, 967; 1914, ii, 105, 107; 1918, ii, 32).

The author has measured the heat of reaction of varying proportions of sodium hydroxide on different oximes and of excess of hydrochloric acid on the same oximes, and on these results bases a discussion of the constitution of the oximes and their relationship to the diazonium hydroxides. The heats of reaction indicate that α-benzaldoxime is more strongly acid than β-benzaldoxime, and in this respect closely resembles acetaldoxime. Accordingly, for the two oximes the following structures are suggested:

$$\begin{array}{cc} \mathrm{Ph{\cdot}C{\cdot}H} & \mathrm{Ph{\cdot}C{\cdot}H} \\ \Vert & \Vert \\ \mathrm{N{\cdot}OH} & \mathrm{HO{\cdot}N} \\ \beta\text{-}. & \alpha\text{-}. \end{array},$$

and from these the structures of the diazo-compounds are deduced as follows, the *iso*-form being more acid than the normal form:

$$\begin{array}{cc} \mathrm{Ph{\cdot}N} & \mathrm{Ph{\cdot}N} \\ \Vert & \Vert \\ \mathrm{N{\cdot}OH} & \mathrm{HO{\cdot}N} \\ \text{Normal.} & \textit{iso.} \end{array}.$$

Finally the author puts forward the hypothesis that in certain compounds containing nitrogen the atom (or atoms) undergo a deformation, the three valencies of nitrogen being displaced, and the atom loses one of its planes of symmetry. This deformation is accompanied by an increase of acidity. Thus there is:

$\overset{R}{\underset{H}{}}\!\!>C{:}NOH$	R·N:N·OH
Unstable form of aldoxime.	Normal diazonium hydroxide.
$\begin{array}{c} R\cdot C\cdot H \\ \Vert \\ HO\cdot \mathbf{N} \end{array}$	$\begin{array}{c} R\cdot \mathbf{N} \\ \Vert \\ HO\cdot \mathbf{N} \end{array}$
Stable form of aldoxime.	*iso*Diazonium hydroxide.

the nitrogen atom indicated by **N** having undergone deformation.

In a final chapter the author discusses the relative merits of Cain's and Blomstrand's structural formulæ for diazo-compounds, and quotes certain facts which, in his opinion, are opposed to Cain's formula. At the same time he considers that Blomstrand's formula does not offer an explanation of all the known properties of the diazo-compounds. W. G.

Condensation Products from *p*-Aminoazobenzene and Ketones or Aldehydes. G. Reddelien (*Ber.*, 1920, **53**, [*B*], 340—344).—Benzophenone is scarcely affected by being heated with *p*-aminoazobenzene even after addition of hydrobromic acid (compare this vol., i, 315); reaction, however, occurs readily if benzophenoneanil (A., 1913, i, 1203) is substituted for the ketone, the necessary condition consisting in the removal of the liberated aniline, which is readily effected by performing the operation in a vacuum at 180°; the p-*diphenylmethyleneaminoazobenzene*, $CPh_2{:}N\cdot C_6H_4\cdot N_2\cdot Ph$, forms coarse, orange-yellow crystals, or, less frequently, large, less intensely coloured plates, both varieties having m. p. 123°. It yields an orange-red *monohydrochloride* and a dark red *dihydrochloride*, both of which are rapidly decomposed by traces of moisture into aminoazobenzene hydrochloride and benzophenone. p-*Fluorenylideneaminoazobenzene*, long, orange-yellow, strongly dichroic needles, m. p. 141—142°, is prepared similarly.

For comparative purposes, the following condensation products of aldehydes and *p*-aminoazobenzene have been prepared: p-*cinnamylideneaminoazobenzene*, $CHPh{:}CH\cdot CH{:}N\cdot C_6H_4\cdot N_2\cdot Ph$, orange-yellow leaflets, m. p. 137—138° (*hydrochloride*, orange-red, crystalline powder); p-*dimethylaminobenzylideneaminoazobenzene*, orange-yellow crystals, m. p. 174—175°; *di*-p-*dimethylaminophenylmethyleneaminoazobenzene* $(NMe_2\cdot C_6H_4)_2C{:}N\cdot C_6H_4\cdot N_2\cdot Ph$, orange-red needles, m. p. 232—233°. The halochromic phenomena on solution in concentrated sulphuric acid are shown in the following table:

	Colour of substance.	Colour of solution.
Benzylideneaminoazobenzene............	orange-yellow.	orange-red.
Cinnamylideneaminoazobenzene........	orange-yellow.	purple-red.
Diphenylmethyleneaminoazobenzene.	orange-yellow.	orange-red.
Fluorenylideneaminoazobenzene	orange.	cinnabar-red.
p-Dimethylaminobenzylideneaminoazobenzene	orange-yellow.	orange-yellow.
Di-p-dimethylaminophenylmethyleneaminoazobenzene	orange.	orange.

It appears, therefore, that the halochromy is noticeably increased when the C:N-group is conjugated with a neighbouring C:C-group, a phenomenon which is also observed with unsaturated anils and ketones. Similarly, the hydrochloride is rendered more stable by the presence of the conjugated C:C-group. The non-appearance of halochromy in the two instances last mentioned is probably attributable to the smaller basicity of the aminoazobenzene residue as compared with the anil residue; as a consequence, salt formation may occur at a dimethylamino-group and therefore not cause halochromy. H. W.

A New Method for Preparing Esters of Amino-acids. Composition of Caseinogen. FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1919, **13**, 378—397).—The outlines of the process are as follows: The amino-acids are converted into their dry lead salts, which are suspended in absolute alcohol and converted into the ethyl esters by saturation with dry hydrogen chloride. After removal of the free hydrochloric acid and the alcohol, the ester hydrochlorides are dissolved in dry chloroform, and the free esters liberated by shaking the solution with anhydrous barium hydroxide. The chloroform is removed by evaporation under reduced pressure, and the esters are dissolved in anhydrous ether. Subsequently they are fractionally distilled in the usual manner. This process avoids considerable loss of esters by hydrolysis, which occurs by the use of aqueous solutions in the usual procedure. This method has already yielded results of value, in that some of the deficit in the amino-acid content of caseinogen has been accounted for. The author gives the following details of the percentage composition of caseinogen, partly from the results of his own work and partly from other sources: Glycine, 0·45; alanine, 1·85; valine, 7·93; leucine, 9·7; proline, 7·63; phenylalanine, 3·88; glutamic acid, 21·77; aspartic acid, 1·77; new syrups, 14·34; lysine, 7·62; histidine, 2·5; arginine, 3·81; tryptophan, 1·5; serine, 0·5; tyrosine, 4·5; hydroxyproline, 0·23; diaminotrihydroxydodecanic acid, 0·75; ammonia, 1·61; sulphur, 0·76; phosphorus, 0·85; substances of peptide nature obtained on hydrolysis, 3·41; total, 97·36%. J. C. D.

Dissociation of Oxyhæmocyanins. CH. DHÉRÉ and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1919, **82**, 1038—1040; from *Chem. Zentr.*, 1920, i, 176—177).—Careful experiments with solutions of pure crystalline oxyhæmocyanin, in some cases in the presence of an antiseptic, show that the substances obtained from the snail and the lobster are readily reducible by physical dissociation. H. W.

A Compound of the Hæmocyanin of the Snail with Nitric Oxide. CH. DHÉRÉ and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1919, **82**, 1041—1043; from *Chem. Zentr.*, 1920, i, 177).—A solution of the hæmocyanin forms with nitric oxide a crystalline, green dye, which is designated "hæmocyanin nitric oxide." H. W.

Liquefaction of Gelatin by Salts. T. R. BRIGGS and EVELYN M. C. HIEBER (*J. Physical Chem.*, 1920, **24**, 74—75).—Solutions of 5% gelatin were mixed with 33% solutions of zinc chloride, potassium chloride, ammonium nitrate, potassium thiocyanate and magnesium chloride, and with saturated solutions of potassium nitrate and ammonium chloride respectively, and placed in a thermostat at 19°. After thirty minutes the mixture containing potassium chloride had set to a jelly, in twenty-four hours those containing magnesium chloride and ammonium chloride had set, and after thirty-six hours the remainder were still liquid. After dialysis for twenty-four hours the whole of the solutions had set, and on again mixing with zinc chloride, ammonium nitrate, and potassium thiocyanate respectively the jellies liquefied within an hour. It is thus proved that the processes of liquefaction and gelatinisation produced by salts are strictly reversible. J. F. S.

Presence of Invertase in the Pure Honey of Bees. ALIN CAILLAS (*Compt. rend.*, 1920, **170**, 589—592).—By the general method of preparation of enzymes by precipitation with alcohol, invertase was isolated in the form of its aqueous solution from a sample of honey. The honey contained approximately 0·05% of the enzyme, which gave all the tests for invertase, including the hydrolysis of sucrose. W. G.

A Method of Testing the Amylolytic Action of the Diastase of Aspergillus Oryzæ. SELMAN A. WAKSMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 293—299).—The Lintner method for measuring the saccharogenic action of different enzymes on starch should not be used for comparative studies with different enzymes, since the end-products are not the same in the various cases. The starch liquefying (iodine) methods, with the exception of that of Wohlgemuth, do not give the "liquefaction" of starch by enzymes, but measure the reduction of the starch to substances giving no longer any reaction with iodine, which is arbitrary. In the study of the action of enzymes on the starches present or embodied in textiles (process of de-sizing), the Lintner method and its various modifications are unsuitable, since the problem consists in the elimination of starch, and not in the production of sugar. A convenient method for measuring the starch-liquefying power (amyloclastic action) of enzymes consists in adding the requisite amount of the latter to 10 c.c. of a 2% paste of raw potato starch, which is maintained at 40°, and observation of the time required for the liquid to become clear; the determination of the end-point may be facilitated by staining the starch, preferably with neutral red. When the stage of hydrolysis corresponding with this end-point is tested with iodine, it is found to be identical with that at which no heavy blue colour is obtained, but only a deep brown to faintly violet-brown colour or faint bluish-violet colour, showing that all the starch paste has been transformed into dextrins.

Comparing the starch-liquefying powers of malt enzymes and

enzymes obtained from *Aspergillus oryzae* (water extract used known commercially as polyzime), the first are found to give a higher Lintner value, whilst the second give a higher liquefying value. The ratio of the latter to the former in the case of malt preparations is 1:4 to 1:5, whilst in the case of *Aspergillus oryzae* enzyme it is 1:1 to 1·5:1, so that the liquefying power of the latter in comparison to its saccharogenic power is four to six times as great as that of the malt preparations. H. W.

Consecutive Action of Two Types of Emulsins on Amygdalin. J. Giaja (*Compt. rend. soc. biol.*, 1919, **82**, 1196—1198; from *Chem. Zentr.*, 1920, i, 299. Compare A., 1914, i, 1099).—If the action of emulsin of almonds on amygdalin is stopped by heating at a period when a portion of the latter remains unattacked, the action can be completed by the subsequent addition of the digestive juice of *Helix pomatia*; the same amounts of hydrocyanic acid and dextrose are formed as when complete decomposition is effected by one ferment only. If the order of addition is reversed, that is, if the emulsin of almonds is added to the amygdalin solution which has been partly decomposed by *Helix* juice and then heated, complete decomposition does not occur, although a certain amount of hydrocyanic acid and of dextrose is formed. Intermediate products are formed under the influence of *Helix* juice which are not further attacked by emulsin of almonds. H. W.

Bivalent Tin as Chromophore in Aromatic Stannous Compounds and the Preparation of Hexa-aryldistannanes. Erich Krause and Reinhard Becker (*Ber.*, 1920, **53**, [*B*], 173—190).—Alkyl compounds of bivalent tin have been described previously, but their isolation in the pure state has proved impossible. The authors have therefore turned their attention to the corresponding di-aryl compounds, which are found to be stable, crystalline substances. Their most remarkable properties are their intense colour, which must be attributed to the unsaturated tin atom behaving as a chromophore, and their peculiar transformation into hexa-aryl distannanes analogous to the hexa-alkyl compounds described by Grüttner (A., 1918, i, 159).

Tin diphenyl is prepared by the addition of finely-powdered stannous chloride to an ethereal solution of a considerable excess of magnesium phenyl bromide; it forms a bright yellow, voluminous, amorphous powder, which has m. p. 130° (to a dark red, viscous liquid), after softening at 126°. Dilute solutions of the substance in benzene are intense yellow to reddish-yellow, and become cloudy and gradually decolorised on exposure to air. The benzene solution becomes dark red, and gives a yellow precipitate on exposure to sunlight. Dry tin diphenyl is rapidly decolorised on exposure to light and air, but it may be preserved unchanged for months in an atmosphere of nitrogen. The freshly prepared material appears to have a normal molecular weight in benzene

solution, but polymerisation soon begins, so that, after a few days, the molecular weight has increased fivefold. In chloroform solution tin diphenyl rapidly absorbs the calculated quantity of bromine and yields tin diphenyl dibromide, which, for purposes of identification, was converted by potassium fluoride into the more readily purified *tin diphenyl difluoride*, colourless, four-sided rods, m. p. above 360°.

Hexaphenyldistannane is prepared by the treatment of stannous chloride with a large excess of magnesium phenyl bromide at 100°, by the action of sodium on tin triphenyl chloride, or by reduction of the latter with sodium and alcohol; it crystallises in colourless, rectangular plates, m. p. 237° (corr.) (from benzene in colourless, shining rhombohedra $+1\cdot5C_6H_6$), and is completely stable towards air. It has a normal molecular weight in benzene solution. It immediately reduces silver solutions to metallic silver, even at −75°. It is converted by bromine in chloroform solution at −30° into tin triphenyl bromide.

Tin di-p-*tolyl* is an orange-yellow, amorphous powder, m. p. 111·5°, after softening at 109°. It is less readily oxidised by air than is tin diphenyl, which, however, it closely resembles in undergoing polymerisation when preserved. Possibly by reason of steric hindrance, tin di-*p*-tolyl, unlike the phenyl derivatives, is not converted into hexa-*p*-tolyldistannane when heated with an excess of magnesium phenyl bromide at 100°; at a higher temperature a complicated decomposition occurs, tin tetra-*p*-tolyl being formed together with many other substances.

Tin tetra-*p*-tolyl (compare Pfeiffer, A., 1910, i. 724) is converted into the monobromide in pyridine solution, and this is transformed into the hydroxide; the latter is purified and transformed by the requisite halogen acid into *tin tri*-p-*tolyl chloride*, coarse, rhombic plates, m. p. 97·5°, *tin tri*-p-*tolyl bromide*, colourless rhombohedra, m. p. 98·5°, and *tin tri*-p-*tolyl iodide*, colourless, rhombic plates, m. p. 120·5°. *Tin tri*-p-*tolyl fluoride*, slender, interwoven needles, m. p. 305°, and *tin triphenyl fluoride*, colourless, minute prisms, m. p. 357°, after darkening at 345°, are also described. The latter substance is of interest, since it is so sparingly soluble in cold alcohol, ether, or water that the chloride can be used for the quantitative precipitation of fluorides. *Hexa*-p-*tolyldistannane*, colourless, rhombic platelets, m. p. 145° (corr.), is prepared by the reduction of tin tri-*p*-tolyl bromide with sodium and alcohol.

Tin tetra-m-*tolyl* forms colourless needles, m. p. 128·5°.

The following *o*-tolyl derivatives were prepared from the product obtained by the action of stannic chloride on the quantity of magnesium *o*-tolyl bromide calculated for the formation of tin tetra-*o*-tolyl (instead of a considerable excess, as recommended by Krause and Schmitz, this vol., i, 198); the crude material was purified by conversion into the hydroxide, which was subsequently converted into *tin tri*-o-*tolyl chloride*, colourless, pointed prisms, m. p. 99·5°, *tin tri*-o-*tolyl bromide*, compact, rhombic plates, m. p. 99·5°, and *tin tri*-o-*tolyl iodide*, hard, rhombic crystals, m. p. 119·5°.

Tin di-p-*xylyl*, m. p. 157°, after softening at 155°, closely resembles the corresponding di-*p*-tolyl compound, but is considerably more stable towards air, so that it may be preserved exposed to air for some considerable time without undergoing change. The following *p*-xylyl derivatives are obtained in the usual manner: *tin tetra*-p-*xylyl*, colourless, microscopic, four-sided rods or cubes, m. p. 278° (corr.); *tin tri*-p-*xylyl chloride*, colourless, compact crystals, m. p. 141·5° (corr.); *tin tri*-p-*xylyl bromide*, large, six-sided crystals, m. p. 151° (corr.); *tin tri*-p-*xylyl iodide*, large, six-sided plates, m. p. 159·5° (corr.); *tin tri*-p-*xylyl fluoride*, slender, microscopic needles, m. p. 247° (corr.); *hexa*-p-*xylyldistannane* (from tin tri-*p*-xylyl bromide and sodium), colourless, rhombic plates, m. p. 196° (corr.).

Tin tetra-m-*xylyl* forms long, rhombic needles, m. p. 224° (corr.); it is isolated with greater difficulty than are its isomerides owing to its greater solubility. The tin tri-*m*-xylyl haloids do not crystallise with the exception of the *fluoride*, slender, interwoven needles m. p. 209° (corr.).

Tin di-α-naphthyl resembles the corresponding xylyl compound in preparation and properties, but is even less sensitive to air; it has m. p. 200° after softening at 196°. H. W.

Physiological Chemistry.

The Action of Certain Precipitates on the Solution of Red Globules. ARTHUR VERNES and ROGER DOURIS (*Compt. rend.*, 1920, **170**, 528—529).—The property, which the serum of pig's blood possesses, of dissolving the red globules from sheep's blood, can be destroyed by dissolving in the serum a precipitate formed from ferric thiocyanate and human serum. W. G.

The Physiological Action of Calcium. R. HÖBER (*Pflüger's Archiv*, 1917, **166**, 531—608; from *Physiol. Abstr.*, 1917, **2**, 523). —The effect of Ca (ions) in diminishing hæmolysis by narcotics is shared by the ions Sr, Ba, and Mg. Mn and Co are more efficacious, than the above, and Ni more efficacious than any of the others. When, however, hæmolysis is produced by hypotonic solutions of sodium chloride, Ca is the most and Ni the least efficacious. When hæmolysis is produced by saponin, the relative inhibitory effect of the ions in question differs with the blood of different animals. In preventing (or diminishing) the toxic action of potassium on skeletal muscle, the ions work in the following order: Ca>Sr>

Mg>Co>Ba>Mn>Ni>Zn, that is, their value corresponds with that in diminishing hæmolysis by hypotonic solutions. In preventing (or diminishing) the toxic action of narcotics on muscle, the ion series reads: Ni>Co, Mn, Ba>Sr, Ca. Further, in preventing (or diminishing) the fibrillar contractions evoked by solutions of sodium chloride, the series becomes: Ni, Co>Mn>Ca, Mg>Sr>Ba. The effect of potassium on the demarcation current of muscle is inhibited not merely by Ca, but also by Sr, Ba, Co, Mn, and Ni ions, but not by Mg. Complex cobalt and chromium ions act like Ca when they are bi- or ter-valent, but not when they are univalent. Cu, UO_2, and Cd cannot replace calcium at all; Zn, Ni, and Ce ions can only do so partly. J. C. D.

Theory of Odour. HANS HELLER (*Biol. Zent.*, 1919, **39**, 364—370; from *Chem. Zentr.*, 1920, i, 139).—Chemical and physiological considerations lead the author to consider Teudt's theory (A., 1913, i, 607) untenable. H. W.

Polonium Radiation and Recovery of Function. H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 383—385).—The effect of α- or β-rays in restoring cardiac action (A., 1917, i, 241) appears to be due to the direct action of the rays, rather than to their influence in determining the liberation of potassium ions from the cardiac muscle. Thus the beating of a frog's heart, which had ceased owing to removal of potassium ions from the circulating liquid, was restored when the organ was exposed to β-rays from polonium, but ceased again when potassium ions were supplied in addition, owing to the opposing effects of α- and β-rays (A., 1918, i, 326). It revived, however, when either the polonium or the potassium ions were removed. J. K.

Permeability of the Glomerular Membrane to Stereoisomeric Sugars. H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 351—359).—Previous investigations (A., 1919, i, 187) gave results which led the author to suspect that the retention of dextrose by the glomerular membrane was in some manner connected with the configuration of the sugar molecule. The hypothesis that the group $\begin{matrix}\mathrm{C{\cdot}OH}\\ \mathrm{H{\cdot}\overset{|}{C}{\cdot}OH}\end{matrix}$ causes retention cannot be true, for *l*-arabinose and *l*-mannose pass through the kidney, whilst *d*-galactose, *l*-xylose, and *d*-ribose are partly retained. Of all the sugars examined (hexoses and pentoses) only dextrose is completely retained by the glomerular membrane. J. C. D.

The Partial Permeability of the Glomerular Membrane to *d*-Galactose and some other Multi-rotatory Sugars. H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 360—373).—The multi-rotatory sugars can be divided into three groups according to their behaviour in the kidney. The first group consists of those sugars of which both modifications are retained by the glomerular membrane. Of this class only one

representative, dextrose, is known. The second group (*d*-galactose, *d*- and *l*-xylose, and *d*-ribose) are partly diffusible through the renal glomerulus, and apparently only one modification is retained. The third class consists of sugars, both modifications of which pass the glomerulus, such are *l*-glucose, *d*-mannose, *d*- and *l*-arabinose. In the case of the members of the second group, the retention or non-retention is governed wholly by the positions which the H and OH linked to the asymmetric C-atom occupy relatively to each other. J. C. D.

The Active Principles of the Pituitary Gland. HAROLD WARD DUDLEY (*J. Pharm. Expt. Ther.*, 1919, **14**, 295—312).—The dried and powdered gland is extracted with acidified water, and the extract purified by precipitation with colloidal ferric hydroxide. From the filtrate, by continuous extraction with butyl alcohol under reduced pressure, crystalline fractions may be obtained which possess strong physiological activity. The extract contains all the uterine stimulant, together with some of the pressor substance and contaminating substances. The view expressed by Abel and Kubota (A., 1919, i, 506) that histamine is identical with the uterine stimulant of the pituitary gland, is not confirmed. Considerable differences in the properties of these substances were observed. J. C. D.

Influence of Temperature on Narcosis of Muscle and Nerve. R. HÖBER (*Pflüger's Archiv*, 1919, **174**, 218—232; from *Physiol. Abstr.*, 1919, **4**, 184).—The depression of irritability of muscle and of conductivity in nerve by the action of various narcotics is increased by warmth and diminished by cold. The effects of potassium chloride, cocaine, and novocaine on muscular irritability are independent of temperature. The dependence of the partition coefficients of indifferent narcotics on temperature has no apparent relationship to their narcotic powers J. C. D.

Carcinolytic Organic Acids. ERNST FREUND and G. KAMINER (*Wien. klin. Woch.*, 1919, **32**, 1105; from *Chem. Zentr.*, 1920, i, 135—136).—Normal serum and normal tissue contain a fatty acid compound which is able to destroy cancerous cells, and is to be regarded as the protective substance of normal cells; it is termed the "normal acid" by the authors. Cancerous serum and tissue show a lack of normal acid, and contain in its place an unsaturated fatty acid compound which behaves as a protective material to the cancerous cell; to this the name *carcinomic acid* is assigned. At least ten times as much normal as carcinomic acid is necessary for neutralisation. Since the preparation of considerable amounts of normal acid is a matter of difficulty (5 litres of serum yield 0·1 gram of acid), the authors have attempted to replace it by acids that can be synthesised. Under similar conditions, oxalic and malonic acids are inactive, succinic acid is active, glutaric, adipic, and pimelic acids are inactive, suberic acid is again active, whilst azelaic and sebacic acids have no action. These results and those

of other experiments lead to the conclusion that the methylene group has a distinct influence on carcinolytic activity. Actually, decane-$\alpha\kappa$-dicarboxylic acid has the power of destroying cancerous cells. The minimal concentrations for succinic, suberic, and decane-$\alpha\kappa$-dicarboxylic acids are about 0·05%, 0·01%, and 0·005% respectively; a parallelism thus appears to exist between increase in activity and number of C_2H_4-groups. In connexion with carcinomic acid, the protective action of sterically different fatty acids towards cancerous cells has been examined. Among isomeric acids, only those substances have a protective effect in which two carboxyl groups must be assumed to be in close proximity to one another and to a carbon atom. H. W.

Significance of Potassium in the Organism. H. ZWAARDEMAKER (*Pflüger's Archiv*, 1918, **173**, 28—77; from *Physiol. Abstr.*, 4, 80).—A summary and extension of previous work (see A., 1917, i, 241; 1918, i, 326, ii, 182) on the replacement of potassium by equiradio-quantities of other elements. Irradiation from without can replace the addition of other radio-active elements to nutritive fluids, and it is immaterial which rays are used for this, except that they cannot be used together effectively, as they are then biologically antagonistic. The equilibrium necessary for proper activity is altered by eosin and by calcium, and in the opposite direction, by fluorescein, and in summer it is immaterial whether the radio-active element which replaces potassium be present in ionic form or as a colloid complex. A frog's heart under the influence of uranium is incapable of giving extra systoles in response to electrical excitation. J. C. D.

Genesis of Thiocyanic Acid in Animals. VIII. SERAFINO DEZANI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 148—160. Compare A., 1919, i, 506).—With man and the dog, just as with the rabbit, ingestion of cauliflower is followed by more or less intense elimination of thiocyanic acid in the urine. The thiocyanogenetic substance of the cauliflower is found also in the white and green forms of *Brassica oleracea L. var. capitata*. This substance appears to belong to the group of so-called extractive substances, as it is neither a protein nor an amino-acid precipitable by phosphotungstic acid, nor a thiocarbimide, nor an organic sulphide. The extractive substances of flesh contain no thiocyanogenetic substances. T. H. P.

The Important Rôle of Preluciferin. RAPHAEL DUBOIS (*Rép. pharm.*, 1919, [3], **30**, 289—291. Compare A., 1897, ii, 112; Harvey, A., 1917, i, 365; 1919, i, 299; this vol., i, 202, 203).—The author objects to the terms photogenin and photophelein for luciferase and luciferin. Luciferase is the enzyme and luciferin the substrate concerned in biochemical oxidations with the production of light; both are thermolabile. The luciferin is used up in the reaction which produces light; but a further supply may

be made by the action of another enzyme, coluciferase, on preluciferin, which is thermostable and quite probably is an albumose. If a solution containing both luciferase and coluciferase be kept at 65°, the luciferase is destroyed. The coagulum is removed from the solution by filtration; the filtrate is mixed with a boiled solution which contains preluciferin; no light is produced. On addition of a small crystal of potassium permanganate to this solution to take the place of the destroyed luciferase, light appears at once, since the coluciferase has made luciferin from the preluciferin. Photophelein may be used as a generic name for mechanical, physical, and chemical agents which favour, activate, or excite the reaction between luciferase and luciferin. Such agents are agitation in the presence of oxygen, dilution with aerated water, heat, compounds with an alkaline reaction (ammonia, sodium carbonate, alkaloids, amines), ethyl ether, etc.; these agents have no action on solutions in which potassium permanganate does not disclose a trace of luciferin.

CHEMICAL ABSTRACTS.

Bioluminescence. XII. The Action of Acid and of Light in the Reduction of Cypridina Oxyluciferin. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1920, **2**, 207—213. Compare this vol., i, 202, 203).—The addition of acid to a boiled extract of cypridina (oxyluciferin) causes the formation of a substance (luciferin), which will give light with luciferase. It would seem, however, that the action of bacteria, yeast, muscle cells, etc., on oxyluciferin must be due not entirely to their acid reaction, but to their reducing power as well. The processes which occur in this reaction are compared with the reduction of methylene-blue, and a scheme co-ordinating the various factors which influence this example of bioluminescence is advanced.

J. C. D.

Behaviour of Benzoylpropionic Acid, Phenylethyl Alcohol, and Phenoxyacetic Acid in the Organism of Man and Dog. H. THIERFELDER and E. SCHEMPP (*Pflüger's Archiv*, 1917, **167**, 280—288; from *Physiol. Abstr.*, 1917, **2**, 465).—The first-named keto-acid is reduced to a hydroxy-acid, and of this the *l*-form is largely excreted as such; a portion of it is further changed. The *d*-form is reduced to phenylbutyric acid, and thus is partly, by β-oxidation, converted into phenylacetic acid, which unites with glutamine. A small amount of the keto- or hydroxy-acid is probably excreted in union with glycine. Phenylethyl alcohol is oxidised to phenylacetic acid. Phenylacetaldehyde given subcutaneously is excreted as phenaceturic acid. Phenoxyacetic acid is not a metabolic product. Most of it is recoverable as such in the urine.

J. C. D.

Pharmacological Action of Ketocineole. GUIDO CUSMANO (*Gazzetta*, 1919, **49**, ii, 228—232).—Similar chemical behaviour is shown by camphor and ketocineole, which differ in molecular structure only as regards the nature of the bridge uniting the tertiary

and quaternary carbon atoms. In their physiological effects, however, these two compounds exhibit differences. The psychomotor excitation produced in man and other mammifers by camphor appears only in embryo on administration of ketocineole, and is mostly masked by symptoms in which depression of cerebral activity is prominent. The differences are more distinct in the case of the frog; here the initial curaric action of camphor which prevents the development of the convulsions observed in warm-blooded animals, is not produced by ketocineole. T. H. P.

Influence of Temperature and Concentration on the Toxicity of Solutions, particularly of Electrolytes. O. Hartmann (*Pflüger's Archiv*, 1918, **170**, 585—645; from *Physiol. Abstr.*, 1918, **3**, 573).—In an extensive series of experiments on *Bosmina longirostiris*, O.F.M., a member of the Cladocera, the effect on the duration of life at ten different concentrations of various acids, inorganic salts, organic salts, and alcohols was studied at temperatures of 0°, 13°, 18°, and 30°. Toxicity curves for the various concentrations and temperatures are figured. The toxicity concentration curve resembles more or less closely the adsorption isotherm of the various substances. The specific toxicity of the substances concerned is responsible for the form and the specific course of the curve. The osmotic pressure, however, tends to shorten life in the higher concentrations of the mildly toxic substances, and determines the acute bend above a certain critical concentration in the case of these curves. The diminishing toxicity of the anion and univalent cation series shows a close correspondence with the known series. The toxicity of the individual substances diminishes on dilution in varying degrees; those with similar or identical toxicity concentration quotients show little change in their relative position, whereas those with widely different quotients exhibit the greatest change in their relative toxicity on dilution. A similar formula for the temperature–toxicity curve is given, but its untrustworthiness is indicated by the variety of constants yielded at different temperatures. The relation of the absolute value of temperature-coefficient (Q_{10}) and its peculiar progress were subjected to a very searching analysis. The very high values often observed at the maximum and minimum temperatures are due to complicated physiological changes in the living system, which are rapidly completed on changes at the temperatures in question. Owing to the very different temperature-coefficients and temperature-toxicity coefficients of the various substances, changes in toxicity occur at different temperatures; substances with similar temperature-toxicity quotients maintain their relative position in the series, whereas those with different quotients alter their relation on changes of temperature. The form of the toxicity–concentration curve is sometimes different for different temperatures, as higher temperatures usually determine a more gradual rise in the duration of life on dilution. Hence the adsorption formula constants will apparently be different at different temperatures. The value of the tempera-

ture-coefficient is also apparently influenced by the concentration of the experimental fluid. A general formula, including concentration, temperature, and duration of life, was constructed from the individual formulæ; its accuracy, however, is only approximate, and varies greatly for the various substances. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Butylene Glycol Fermentation of Sugar by *Bacillus anthracis*. M. Lemoigne (*Compt. rend. soc. biol.*, 1919, **82**, 984—986; from *Chem. Zentr.*, 1919, iii, 1018. Compare this vol., i, 122).—Fermentation of sugar by three different varieties of *B. anthracis* gave distillates containing a small amount of a reducing agent which yielded diacetylosazone with phenylhydrazine, and is therefore regarded as acetylmethylcarbinol; $\beta\gamma$-butylene glycol could not be detected. The phenomena are thus analogous to those observed with the *B. subtilis* group; whilst, however, in the latter case the $\beta\gamma$-butylene glycol collects in the cultures, it is immediately transformed by *B. anthracis* into lactic acid, and cannot be detected even as a transitory phase. The author is led to the conclusion that lactic acid and butylene glycol are intermediate products of the same process of fermentation which follows a different course with *B. anthracis* and *B. subtilis.* H. W.

Cycloclastic Power of Bacteria. I. A Quantitative Aerobic Decomposition of Histidine by Bacteria. Harold Raistrick (*Biochem. J.*, 1919, **13**, 446—458).—The bacterial decomposition of histidine was followed by studying the fate of the nitrogen groups. *B. paratyphosus A*, *B. paratyphosus B*, *B. faecalis alcaligenes*, and *B. pyocyaneus* can produce ammonia from both the amino-group of the side-chain and from the iminazole nucleus of the histidine molecule. With *B. proteus vulgaris* ammonia is formed only from the side-chain nitrogen, and it appears probable that this organism cannot break down the ring structure.

J. C. D.

Respiratory Process of Nitrifying Bacteria. III. The Respiration of the Nitrite Organisms and the Influence of Chemical Substances. O. Meyerhof (*Pflüger's Archiv*, 1917, **166**, 240—280; from *Physiol. Abstr.*, 1917, **2**, 207).—The material used was obtained from a pure culture of *Nitrosomonas*, and Winogradsky's solution was employed as a culture medium.

Under favourable conditions cultures were obtained which in twenty-four hours could oxidise 4 grams of ammonium sulphate per litre to nitrite. The rate of respiration depends on the concen-

ration of the ammonium salt, the optimum being at a concentration of $N/200$-NH_4, whilst it is zero in a concentration of $N/10$-NH_4. The accumulation of the nitrite ion retards respiration, and growth stops when the concentration of this ion reaches $0{\cdot}25N$. With decreasing partial pressure of oxygen there is decreasing respiration from about one-third atmospheric pressure downwards. The H-ion concentration strongly influences the respiration rate; the optimum is in a concentration of $P_H = 8{\cdot}4$ to $8{\cdot}8$; outside the limits $P_H = 9{\cdot}4$ and $P_H = 7{\cdot}6$ no respiration takes place.

The rate of respiration is very sensitive to alkali and alkaline-earth salts, and the heavy metals are very toxic. Respiration and growth respond differently towards nitrogen-free organic substances. Dextrose retards growth in $0{\cdot}001M$-solution, but respiration is not retarded in $0{\cdot}2M$. Methyl alcohol is more toxic than ethyl alcohol. J. C. D.

The Free Energy of Biological Processes. GEORGE A. LINHART (*J. Gen. Physiol.*, 1920, **2**, 247—251).—From considerations of energy exchange it is concluded that only about 1% of the total available energy is utilised in the fixation of nitrogen by *Azotobacter*, growing in a 0·1 molar solution of mannitol.

J. C. D.

Nitrogen Metabolism in Saccharomyces cerevisiæ. LESLIE HERBERT LAMPITT (*Biochem. J.*, 1919, **13**, 459—486).—Excess of yeast ensures the removal of the greatest total amount of nitrogen. During active fermentation, the greater the coefficient of multiplication, the greater the amount of nitrogen assimilated by each cell. Active reproduction may result in a lowering of the nitrogen coefficient, but the final coefficient is independent of the initial value, tending to reach a constant value for any particular conditions of reproduction. The action of yeast on asparagine may result in the production of malic acid, the ammonium salt of which is readily fermented, with the production of ethyl alcohol. Propionic acid and its ammonium salt are not fermented (compare Effront, A., 1908, i, 491; 1909, ii, 255). Fermentative activity is essential to nitrogen assimilation, but once induced, the deamination may continue after zymatic activity ceases. During fermentation, yeast loses nitrogen to the medium. This process, which has been termed "nitrogen excretion," is dependent on the life of the cell, and takes place even when nitrogen is being assimilated. The substances which are excreted can be used as a source of nitrogen by the yeast under suitable conditions. Increase in the amount of sugar available increases the rate of excretion, but there is no proportion between zymatic activity and such excretion.

J. C. D.

Influence of Substances Extracted from Yeast on the Fermentation of Carbohydrates by Yeast. EMIL ABDERHALDEN (*Fermentforsch.*, 1919, **3**, 44—70; from *Chem. Zentr.*, 1920, i, 16. Compare Abderhalden and Schaumann, A., 1919, i, 108).—The influence of yeast extract is proved in a series of

experiments in which equal amounts of yeast are allowed to act on equal weights of carbohydrate, and fresh amounts of the latter are added as soon as the evolution of carbon dioxide markedly slackens until further addition does not cause renewed fermentation; in these circumstances, much more sugar is fermented in the presence of alcoholic yeast extract than is otherwise the case. Simultaneously, the rate of fermentation is greatly increased, generally to a considerably greater extent than by fructosediphosphoric acid. The yeast cells also increase more rapidly, but the greater activity which is thus indicated is not sufficient to account entirely for the action of the yeast extract, since the activating effect is also observed when expressed juice or dry yeast is used. H. W.

Observations on Yeast (mainly Munich Brewery Press Yeast). T. Bokorny (*Pflüger's Archiv*, 1916, **164**, 203—273; from *Physiol. Abstr.*, 1916, **1**, 453).—In keeping with the fact that sucrose is more readily fermented than dextrose, the previous treatment of yeast with antiseptics destroyed its capacity to ferment the latter, but not the former sugar or maltose. Glycerol may be included among the adequate sources of carbon for the growth of yeast. When added to a nutrient medium containing sugar, ammonium sulphate, and salts, an increase of 30 to 42% in the dried weight was observed at the end of three days, as compared with 9% in the control culture. The substitution of peptone or amino-acids for the ammonium salt gave similar results. Although the capacity of furnishing the aldehyde atom-complex is probably the determining factor in the utilisation of carbon, formaldehyde and other aldehydes were not assimilated by the yeast cell.

Peptone is an excellent source of nitrogen, and its addition to a medium containing sugar and salts resulted in an increase of 163% in the dried weight after the lapse of three days; glycine was the least satisfactory of the amino-acids examined, and yielded an increase of only 19%.

Although large quantities of fat have been found in involuting yeast, no appreciable increase in the fat content occurred even when yeast was cultivated in the most favourable medium (peptone and sugar solution).

The study of certain injurious factors showed that yeast was not destroyed by freezing or by drying at the ordinary temperature for eight days; prolonged drying killed the yeast, but did not destroy the zymase. Neutral salts in saturated solution usually prevented fermentation within a few days. The injurious effects of a number of organic and inorganic acids, both on the cell and on zymase activity, are recorded. J. C. D.

The Chemistry of Alcoholic Fermentation. Ernst Zerner (*Ber.*, 1920, **53**, [*B*], 325—334).—The author gives an account of the manufacture of glycerol by the Connstein-Lüdecke process (A.,

1919, i, 463) during the war in Austria-Hungary, which is also of interest, since some of the conclusions are at variance with those arrived at by Neuberg and Reinfurth (this vol., i, 125). The most important results are as follows. Equivalent amounts of glycerol and acetaldehyde are produced in the process; in addition, alcohol and carbon dioxide are formed, and these are the only substances obtained in appreciable amount. Increase in the amount of sodium sulphite increases the yield of glycerol and acetaldehyde, but more than 38% of glycerol cannot be obtained. Sodium sulphite may be replaced by sodium hyposulphite. Failure to produce glycerol in quantitative amount by sufficiently increasing the relative proportion of sulphite has been attributed by Neuberg to dissociation of the aldehyde–bisulphite compound; this conclusion appears to be unfounded, since with moderate additions of sulphite the equivalent amount of glycerol is almost obtained, whilst with very large additions (which should have the effect of suppressing dissociation of the aldehyde–bisulphite compound) the yield of glycerol sinks to about two-thirds of that theoretically possible. The effect seems rather to be attributable to the fact that action between aldehyde and bisulphite is not an instantaneous process, and that a certain amount of opportunity is thus offered for further degradation of the aldehyde and glycerol to alcohol and carbon dioxide.

At first sight, it seems reasonable to suppose that pyruvic acid is an intermediate stage in the fermentative conversion of sugar into aldehyde and glycerol, and Neuberg has shown that the acid can actually be fermented in the presence of sulphite. In these experiments, he has only used one-eighth to one-fourth the equivalent amount of the sulphite; the use of larger proportions, however, shows that the bisulphite compound of pyruvic acid is not fermentable, and that neither pyruvic nor glyceric acid can constitute the intermediate stage in the production of aldehyde by alcoholic fermentation.

When sugar is fermented in the presence of sodium thiosulphate, sulphur is soon precipitated, hydrogen sulphide is evolved, and, after a time, fermentation ceases: the yield of glycerol, reckoned on the sugar actually fermented, is very considerable. When the experiments are repeated with the addition of sodium sulphite or sodium hydrogen carbonate, reaction proceeds as if the thiosulphate were not present. It appears, therefore, that an acid is produced during fermentation which decomposes the thiosulphate according to the equation $Na_2S_2O_3 + HX = NaHSO_3 + NaX + S$. The sulphur is converted into hydrogen sulphide by the reducing action of the yeast, whilst the sodium hydrogen sulphite combines with the aldehyde, and thus provides the possibility of a good yield of glycerol. Fermentation is stopped owing to the production of organic sulphur derivatives, which poison the yeast. In the presence of sulphite or carbonate, the acid is neutralised by these, and the thiosulphate remains undecomposed. Generally, it may be stated that glycerol and aldehyde are intermediate products of

alcoholic fermentation which are simultaneously formed, and, in normal circumstances, simultaneously disappear; as a preliminary phase, an acid must be formed, which, however, is not identical with pyruvic acid.

During normal fermentation (without sulphite), the maximum amount of aldehyde appears to be present in the middle period of action. H. W.

The Regulator System: Primary Phosphate-Bicarbonate-Free Carbonic Acid, in place of the System: Primary Phosphate-Secondary Phosphate. W. WINDISCH and W. DIETRICH (*Woch. Brau.*, 1920, **37**, 81—83).—The lowering of surface tension of aqueous solutions of eucupine dihydrochloride, which results from the liberation of the free base by alkalis (compare Traube, A., 1915, ii, 571), has been used as a means of investigating the equilibrium in the reaction $K_2HPO_4 + CO_2 = KH_2PO_4 + KHCO_3$ in dilute aqueous solutions. It is concluded that in presence of excess of carbon dioxide the reaction proceeds practically to completion from left to right. In living and breathing tissues, therefore, and in fermenting liquids, phosphates must be present entirely as primary salts in equilibrium with potassium hydrogen carbonate and carbon dioxide. Only when respiration or fermentation has ceased and there is no longer an excess of carbon dioxide can dipotassium phosphate exist in equilibrium with the monopotassium salt. J. H. L.

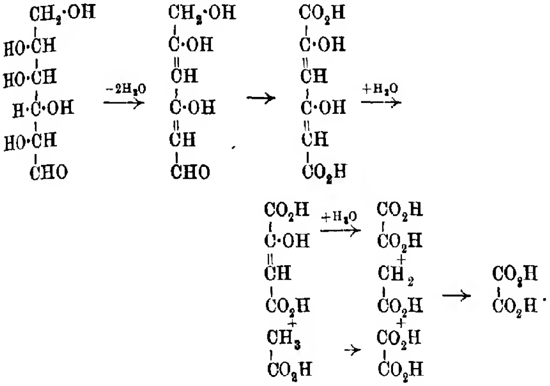
Mechanism of the Formation of Oxalic Acid by Aspergillus niger. HAROLD RAISTRICK and ANNE BARBARA CLARK (*Biochem. J.*, 1919, **13**, 329—344).—Good yields of oxalic acid were obtained when *Aspergillus niger* was grown in the presence of the four-carbon dibasic acids, this being especially true in the case of succinic, fumaric, and malic acids. Very little oxalic acid was produced from sodium maleate, a result which is in agreement with Buchner's observation that *A. niger* can utilise fumaric acid, but not maleic acid, as a source of carbon.

When the four-carbon monobasic acids were examined, there was very little growth of the mould and no production of oxalic acid.

Unexpected results were obtained in the case of the three-carbon acids. In almost all cases there was good growth of the organism, but practically no production of oxalic acid. Of the two-carbon acids, acetic acid behaved differently from glycollic and glyoxylic acids in giving rise to a considerable production of oxalic acid.

Growth of *A. niger* was good in media containing formic acid, but no production of oxalic acid was apparent. A consideration of these results leads the authors to conclude that the breakdown of the sugar molecule by *A. niger* does not take place by a primary splitting of one molecule of sugar into two molecules of a three-carbon acid. Neither can it occur as a gradual breakdown of the molecule carbon by carbon, for this would not give rise to the large yields of oxalic acid unless the micro-organism can synthesise this

acid from one-carbon compounds, and the authors present evidence that this does not occur. The decomposition probably takes place in two stages, and may be illustrated by the following scheme:



The evidence in support of these changes is discussed. J. C. D.

Colloidal Chemistry of Cell Division. JOSEF SPEK (*Koll. Chem. Beihefte*, 1920, **12**, 1—91).—A number of experiments on the effect of salts of lithium, potassium, magnesium, and calcium on the cell division of *Paramœcium caudatum*, *P. aurelia*, and *Stylonichia mytilus* are described. It is shown that salts can either delay or accelerate the cell division by changing the swelling conditions of the colloidal plasma, or they can hinder the division by accumulating in the inside of the cells. Salts which have a very strong influence on the swelling of colloids are also capable of effecting a marked change in the velocity of cell division. Salts which have two ions, each possessing a strong swelling action, accelerate the rate of cell division to a marked extent. Such salts as lithium bromide, lithium chloride, and potassium thiocyanate possess this property to a marked degree. That these salts accelerate the plasma swelling of the *Paramœcia* is seen by the increase in volume of the organisms. Salts which reduce the swelling, such as calcium chloride and the sulphates, retard the cell division to a marked extent. The sulphates increase in their retarding action in the order Li>K>Na. In the case of lithium sulphate, it is possible that the accelerating influence of the cation may outweigh the retarding influence of the anion. In the case of the chlorides, the influence of the cations follows the order Li>Na>Ca, which is the same as the order in which they produce swelling. Potassium chloride, which accelerates the swelling of *Paramœcia* more strongly than sodium chloride, has a much less effect than lithium chloride and potassium thiocyanate, and sometimes it retards the cell division. This is explained by the greater

ease with which this salt passes inside the cells, or, in other words, it is due to a too large increase in salt content of cells in media containing potassium chloride. Sodium chloride has much less power of penetrating the cell wall. The very powerful action of lithium chloride and potassium thiocyanate is due to their coagulating influence on the surface of the cell body without affecting the interior of the cell. In the case of magnesium salts, both the chloride and the sulphate have a very indifferent action, which is due to a slight penetration of the salt. No single experiment points to cell division being effected by the withdrawal of water, that is, cell division is not an osmotic phenomenon. The addition of a substance, capable of swelling, to the culture medium, for example, gelatin, retards the cell division. Different species of *Paramœcia* behave differently towards salts. The difference is attributed to varying permeability of the cells and a dissimilar swelling capacity of the plasma. The experimental results lead to the following hypothesis. The swelling of the plasma colloids, before the cell division, is brought about by the appearance of a base, which is a by-product in the synthesis of the nuclein. The increased permeability during the cell division is accompanied by an increase in the salt content of the cell which compensates the action of the base. An increase in the salt concentration above a given quantity stops the cell division. The formation of substances possessing good swelling properties in the cell occasions new cell division. The swelling of the colloids promotes the gas exchange and the hydrolytic processes in the cell. Every cell division leads more or less completely automatically to further cell divisions. J. F. S.

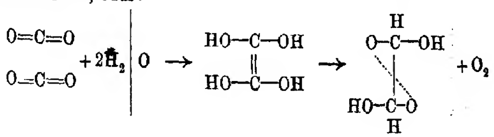
The Glycerophosphatase of Seeds. ANTOINE NĚMEC (*Bull. Soc. chim.*, 1920, [iv], **27**, 153—158).—The author has recently shown (this vol., i, 268) that glycerophosphatase is very widespread in plant cells and in the tissues of ungerminated seeds. It is now shown that this enzyme acts best in an acid medium, the optimum action being obtained with an acidity of approximately 0·06*N*. The velocity of the action which the enzyme produces indicates that it is a bimolecular action. W. G.

The Assimilation Problem. GERTRUD WOKER (*Pflüger's Archiv*, 1919, **176**, 11—38; from *Chem. Zentr.*, 1920, i, 90).—Carbon dioxide is a very inert substance, and, in its ordinary form, is only very slightly attacked by reducing agents. If reaction is to occur, it is necessary for it to suffer change in its molecular structure. "This probably occurs by isomerisation, with the formation either of a primary peroxide, $C{\lll}^{O}_{O}$, or of a secondary peroxide, $C{<}^{O}_{O}$, which, by addition of water, yields $C{<}^{O-OH}_{OH}$." It is found that bicarbonates and carbonates at the moment of their production or disappearance are more reactive than the ordinary

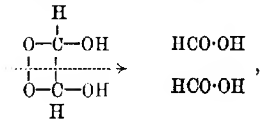
salts. A yellow coloration is produced when a mixture of potassium and sodium hydrogen carbonates and the corresponding normal carbonates in the presence of methyl alcohol is exposed to intense sunlight; the solution reduces Fehling's solution, but the presence of sugar could not be established. The corresponding carbonates and hydrogen carbonates alone do not behave in a similar manner. According to the author, assimilation is made up of a reduction phase and a subsequent combination phase. Assuming the occurrence of isomerisation and the formation of a secondary peroxide, $>C<^{O\cdot OH}_{OH}$, a compound is formed which tends to eliminate oxygen, and thereby to yield the group $>CH\cdot OH$, which is predisposed towards condensation. "Assuming the formation and immediate further utilisation of the unsaturated radicle $>CH\cdot OH$ (which is tautomeric with formaldehyde), a number of difficulties inherent to Baeyer's formaldehyde hypothesis are circumvented without losing the advantages of the latter." The formation of formaldehyde or its desmotrope from methyl alcohol and carbon dioxide can, in the presence of excess of the latter, lead to the production of dihydroxyacetone, which may be of importance for the synthesis of sugars, and, by reduction, for the formation of glycerol. Reductions with methyl alcohol are of considerable interest, since the latter is widely distributed in nature and chlorophyll is an ester of methyl alcohol. The author shows, further, how the following substances may arise by the union of $>CH\cdot OH$ groups in the "condensation-phase": dextrose, lævulose, inositol, the γ-pyrone ring, furfuraldehyde, pyrogallol, quinol, etc. The same group can also react with ammonia, possibly derived from formhydroxamic acid, to yield the alkaloids of the pyrrolidine or piperidine series. The rôle of chlorophyll in assimilation is discussed, the author assuming that it sensitises the isomerisation of the carbon dioxide and acts as a catalyst in the condensation phase; an intermediate union of the $>CH\cdot OH$ group with the magnesium atom of the chlorophyll appears most probable, and explains the formation of optically active substances from initially inactive material, since union occurs with an asymmetric substance, namely, the chlorophyll dye.

H. W.

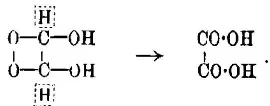
New Theory of Carbon Dioxide Assimilation. P. R. Kögel (*Zeitsch. wiss. Photochem.*, 1920, **19**, 215—223).—A theory of the assimilation of carbon dioxide by plants is put forward. The action of light is to polymerise the carbon dioxide, which with hydrogen then forms tetrahydroxyethylene, which passes over into the keto-form, thus:



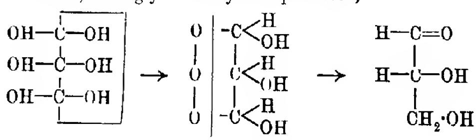
This compound contains the characteristic sugar grouping $\mathrm{HO{-}\overset{H}{C}{-}O}$. The formation of the plant acids, formic and oxalic, is easily deduced from diketoethyl dioxide. In the case of formic acid, it is a simple splitting of the molecule,



whilst in the case of oxalic acid the removal of two hydrogen atoms is necessary.

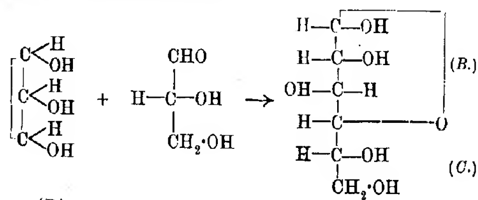


If, instead of two molecules of carbon dioxide, three undergo photo-polymerisation, then glyceraldehyde is produced,



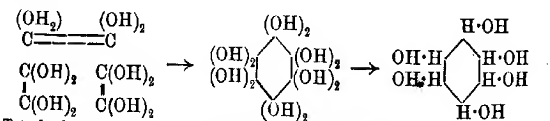
(*B.*)

and the glyceraldehyde combines with *B*, with the loss of three oxygen atoms, to form dextrose.



(*B.*) (*C.*)

The formation of inositol on this hypothesis is represented as follows:



Tetrahydroxyethylene. Dodecahydroxy*cyclo*hexane. Inositol.

J. F. S.

The Absorption of Calcium by the Roots of Plants and its Antitoxic Properties with respect to Copper. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **170**, 420—425. Compare A., 1917, i, 530).—Calcium, even in excess, does not prevent the absorption of copper by the roots of plants or its diffusion into their aerial organs. Similarly, copper does not prevent the assimilation of calcium. The poisonous effect of copper is not due, therefore, to its depriving the young plant of one of its essential nutrients. The antitoxic action of calcium with respect to copper is physiological, and not due to its preventing the penetration of the metal. The explanation probably lies in the fact that the calcium favours the evolution of the plant, giving it greater vigour, and in particular giving it greater volume, into which the copper diffuses, thus preventing, within certain limits, all dangerous accumulation of this latter metal. W. G.

Some Factors Affecting the Concentration of Electrolytes in the Leaf Sap of Syringa vulgaris. T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 651—666. Compare Dixon and Atkins, A., 1916, i, 108).—The determination of the concentration of electrolytes of the cell by means of conductivity observations is unsatisfactory unless allowance is made for the viscosity of the sap, and to this extent Chandler's results (compare *Missouri Agric. Exp. Stat. Res.*, 1914, *Bull.* No. 14) are incorrect. The application of the linear viscosity correction as a means of ascertaining the quantity of electrolytes in the sap is liable to be misleading, and recourse must be had to ascertaining the loss in conductivity which takes place in some salts, such as potassium chloride, after solution in the sap.

Considerable fluctuations in the concentrations of electrolytes in the leaf sap of *Syringa vulgaris* trees growing in different localities have been found. There appears to be a general tendency for the concentration of electrolytes to vary inversely with that of the non-electrolytes. It is suggested that these fluctuations are associated with the rate of carbon assimilation, which determines the rate at which electrolytes are removed from solution in metabolism. It is shown that the concentration of salts in the ascending sap is not responsible for these fluctuations. W. G.

Fat-soluble Vitamine. IV. The Fat-soluble Vitamine Content of Green Plant Tissues, together with some Observations on their Water-soluble Vitamine Content. H. STEENBOCK and E. G. GROSS [with co-operation of MARIANA T. SELL] (*J. Biol. Chem.*, 1920, **41**, 149—162. Compare this vol., i, 274).—Five % of clover or lucerne as the sole source of fat-soluble accessory factor in the diet of a rat will permit normal growth and reproduction. Lettuce, spinach, and chard contain the accessory factor in amounts of the same order, but, of these, lettuce appears to be the poorest. In harmony with the theory that fat-soluble *A* is associated with certain yellow plant pigments is the fact that

cabbage does not contain much of the accessory factor (*loc. cit.*). Fifteen % of lucerne, clover, and cabbage supplied sufficient water-soluble *B* for growth of young rats. J. C. D.

Fat-soluble Vitamine. V. Thermostability of the Fat-soluble Vitamine in Plant Materials. H. STEENBOCK and P. W. BOUTWELL [with co-operation of MARIANA T. SELL and E. G. GROSS] (*J. Biol. Chem.*, 1920, **41**, 163—171).—The fat-soluble vitamine in yellow maize is apparently unaffected by heating three hours under 7 kilos. pressure. Neither does this treatment cause appreciable destruction of the factor as found present in chard, carrots, sweet potatoes, or squash.

No deleterious action of the ensiling process on the fat-soluble accessory factor was detected. The experiments indicate that the accessory substance, as it occurs in grains, leaf and stem tissue, fleshy roots, and curcubitous vegetables, is comparatively thermostable. J. C. D.

The Ability of Plants to Form Optical Antipodes. KURT HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [*B*], 119—129).—See this vol., i, 328.

Occurrence of Chlorogenic Acid in Araliaceæ and Gorter's Reaction. A. W. VAN DER HAAR (*Pharm. Weekblad*, 1920, **57**, 194—195).—Leaves of ordinary ivy (*Hedera helix*) and of various members of the *Araliaceae* were tested for the presence of chlorogenic acid by the method given by Gorter (A., 1909, i, 588). Ivy leaves alone gave a faint positive reaction; the others gave no reaction. The *Araliaceae* examined were of European growth; those which Gorter found to contain chlorogenic acid were obtained from the East Indies (A., 1909, i, 935). W. S. M.

Origin and Transformation of Inulin in Artichoke Tubers. H. COLIN (*Bull. Assoc. Chim. Sucr.*, 1919, 37, 121—126).—The leaves of the artichoke (*Helianthus tuberosus*) are free from inulin at all stages of growth. They contain sugars and starch, and are as rich in starch as the leaves of the potato plant. Formation of inulin takes place in the stem, throughout its whole length, and is completed in the tubers. The inulin must be produced chiefly from dextrorotatory carbohydrates supplied by the leaves. There is practically no difference between young and mature tubers in respect of the nature of the carbohydrates present. The rotatory power of the juice of the tubers undergoes no appreciable change between August and November, but afterwards approaches zero, and finally becomes positive, owing to the conversion of inulin into lævosans of lower molecular weight and the formation of sucrose. When the new plant begins to develop, the inulin passes into the stem chiefly in the form of reducing sugars. J. H. L.

Fatty Acids of Earthnut Oil. A. HEIDUSCHKA and S. FELSER (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 241—265).—The fatty acids

obtained from a specimen of earthnut oil had the following composition: arachidic acid 2·4%, lignoceric acid 1·9%, stearic acid 4·5%, palmitic acid 4·0%, oleic acid 79·9%, and linolic acid 7·4%. The oleic acid probably included a small quantity of hypogæic acid. W. P. S.

Cyanogenesis in Sudan Grass: a Modification of the Francis–Connell Method of Estimating Hydrocyanic Acid. PAUL MENAUL and C. T. DOWELL (*J. Agric. Res.*, 1920, **18**, 447—450).—A determination was made of the amount of hydrocyanic acid in Sudan grass in freshly-cut samples at intervals of a week during the season. The amount obtained was found to be 0·0105% in the fresh plant, only a third of that contained in the grain sorghums. The amount was determined by finely dividing the grass and leaving it with water at 40° for two hours. After this it was made strongly acid with tartaric acid, and distilled into 30 c.c. of 2% sodium hydroxide. The cyanide was precipitated as Prussian-blue, which was burned in a muffle furnace and weighed.

The colorimetric method of Francis and Connell for the estimation of hydrocyanic acid (A., 1913, i, 1284) was investigated and improved, as follows. The distillate containing the hydrocyanic acid is evaporated with 1 c.c. of concentrated yellow ammonium sulphide at 70°. The residue is heated at 130°, dissolved in 10 c.c. of warm water acidified with hydrochloric acid, and calcium chloride solution added drop by drop until the sulphide ceases to form; then 10% ferric chloride solution is added until the red colour is permanent. The solution is then filtered, and 5 c.c. of ferric chloride solution added to the filtrate. The heating at 130° is found to prevent colloidal sulphur going into solution, and the addition of the second quantity of ferric chloride produces the maximum intensity of colour. No change in this intensity is produced by the addition of electrolytes. A standard solution was prepared from a standard solution of potassium cyanide in a similar manner, and the two solutions were compared in a Bock-Benedict colorimeter. J. H. J.

Hydrocyanic Acid Content of Phaseolus lunatus. H. LÜHRIG (*Chem. Zeit.*, 1920, **44**, 166—167).—Beans of the *Phaseolus lunatus* species were found to yield small quantities of hydrocyanic acid when steeped for several hours in water, then macerated, acidified with tartaric acid, and steam distilled. The distillate was collected in dilute silver nitrate solution, and since sulphur compounds also distilled, it was found necessary to dissolve the silver cyanide in ammonia, separate the silver sulphide by filtration, and reprecipitate the silver cyanide by the addition of nitric acid. The silver cyanide was then collected, ignited, and the residue of metallic silver weighed. Nine samples of the beans examined yielded from 5·1 to 23·4 mg. of hydrocyanic acid per 100 grams of beans. The beans did not produce any poisonous effect when eaten in large quantity, provided that they had been

properly steeped in water, washed, and boiled for three hours. Treatment with emulsin during the steeping operation did not increase the amount of hydrocyanic acid yielded to any appreciable extent.

W. P. S.

Constituents of the Seeds of Pharbitis nil chois. Y. Asahina and S. X. Terada (*J. Pharm. Soc. Japan*, 1919, 452, 821).—From the seed of *Pharbitis nil chois* (*P. hederacea chois*, *P. triloba*, Miq., *Ipomea triloba*, Th.) (the Chinese drug "Ch'ien-niu-tzu"), the authors have isolated 3·44% of the resin glucoside pharbitin, m. p. about 145—155°, darkening at 134°, $[\alpha]_D^{17}$ −43·53° (acetyl derivative, m. p. 115—120°, softening at 110°, $[\alpha]_D^{17}$ −18·87°), which yields by hydrolysis (1) a fatty acid which is volatile with steam (possibly a valeric acid with some tiglic acid), (2) the non-volatile *nilic acid* (*barium* salt,

$$C_{10}H_{18}O_6Ba,2H_2O),$$

and (3) pharbitic acid, m. p. 155—162°, $[\alpha]_D^{11}$ −47·61° (Kromer, A., 1897, ii, 68, gives m. p. 156—162° and $[\alpha]_D$ −46·62°). The hydrolysis of pharbitic acid by 5% sulphuric acid yields dextrose, a pentose (osazone, m. p. 172°; possibly methylpentose), and an acid identical with ipurolic acid obtained by Power and Rogerson from *Ipomœa purpurea* (A., 1908, ii, 725).

Chemical Abstracts.

Chemical Constituents of Malt Germs, especially Hordenine. Yoshitaka Hashitani (*J. Tokyo Chem. Soc.*, 1919, 40, 647—667).—The air-dried germs contain water 10·21, ash 3·02, crude protein 21·49, pure protein 13·32, crude fat 3·19, crude fibre 18·40, soluble non-nitrogenous substances 43·69, reducing sugar (calculated as dextrose) 3·65, non-reducing sugar 1·02, pentosan 18·42, methylpentosan 1·05, and cellulose 12·04%. The cell wall is shown by microchemical examination to contain mainly cellulose, which, after hydrolysis with 3% sulphuric acid, responded with tests for xylose, dextrose, lævulose, and galactose. The dried malt germ contains 4·65% of nitrogen. Of the total nitrogen, 6·67% corresponds with water-soluble protein nitrogen, 56·77% with pure protein nitrogen, 20·22% with amino-acid nitrogen, 23·01% with diamino-acid, purine base, and other nitrogen. The air-dried material contains 0·11 of asparagine and 0·13% of hordenine. The sulphate of the latter forms colourless needles, m. p. 209—211°; the hydrochloride has m. p. 176·5—177·5°, the hydrobromide m. p. 173—174°, the hydrogen tartrate m. p. 170—171°, the normal tartrate m. p. 180—181°, the hydriodide m. p. 227—228°, and the methiodide m. p. 179—180°. Benzoylhordenine, m. p. 47—48°, forms a hydrobromide, m. p. 171—172°, and a sulphate, m. p. 270—271°.

Alcoholic fermentation is accelerated by the addition of 0·005%, but is stopped completely by 1·28% of hordenine.

Chemical Abstracts.

General and Physical Chemistry.

The Optics of Disperse Systems. IV. I. LIFSCHITZ and GEORG BECK (*Kolloid Zeitsch.*, 1920, **26**, 58—66. Compare A., 1918, ii, 181, 253; this vol., ii, 137).—The chemical processes occurring during change in the colloidal state and their effect on the change in the light absorption is theoretically considered. An attempt is made to use the published work on the refractometric measurements of colloids to explain the rôle of the change in the colloidal state in the change in light absorption. The density, refractive index, molecular and specific refractivities for the *C*, *D*, and *F* lines have been measured for solutions of twenty organic acids and their sodium salts in methyl alcohol at 25°. It is shown that the increase in refraction from acid to sodium salt is different in the different cases, but with acids which form salts accompanied by a rearrangement or by exercising subsidiary valencies there is an extraordinarily large change. The increase in refraction in salt formation is independent of simultaneous peptisation or colloid formation, and an abnormally large increase in the refraction cannot be explained by a change in the dispersity. It is also shown that a very large percentage of cases of vario-chromism and polychromism are to be explained by intramolecular action of subsidiary valencies, and that chromoisomerism is to be similarly explained. J. F. S.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. V. Alkyloxyacetic Acids. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 8, 1—7; from *Chem. Zentr.*, 1919, iii, 987. Compare this vol., ii, 129).—The alkyloxyacetic acids exhibit optical values slightly lower than that of acetic acid itself. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VI. Esters of Keto-alcohols, $COMe\cdot[CH_2]_n\cdot O\cdot CO\cdot Me$. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 8, 1—7; from *Chem. Zentr.*, 1919, iii, 987).—Further investigation with fresh materials shows that the optical values increase somewhat with increase in the relative distance between the carbonyl group and that of oxygen connected to two carbon atoms in the cases of esters of the lower alkyloxy-aliphatic acids and keto-alcohols. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VII. Ether-Alcohols, $RO\cdot[CH_2]_n\cdot OH$. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [*A*], 10, No. 9, 1—8; from *Chem. Zentr.*, 1919, iii, 981).—Spectrochemical investigation of the monomethyl, ethyl, and propyl ethers

of ethylene glycol and of the monomethyl and ethyl ethers of trimethylene glycol shows these compounds to be closely related optically. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VIII. Mutual Spectrochemical Action of Hydroxyl Groups. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 10, 1—10; from *Chem. Zentr.*, 1919, iii, 981).—Investigation of ethylene and trimethylene glycols showed that two hydroxyl groups in direct union with one another cause marked exaltation, which is progressively diminished by the successive introduction of methylene groups between the hydroxyls. Certain atoms or atomic groups directly united with one another cause optical exaltation ($HO \leftarrow \rightarrow OH$, $O \leftarrow \rightarrow O$, $-S \leftarrow \rightarrow S-$, $-Se \leftarrow \rightarrow Se-$), whilst others bring about depression

$$(C \rightarrow \leftarrow (OR)_{2, 3, 4}, H_2N \rightarrow \leftarrow NH_2, N \rightarrow \leftarrow N),$$

a third section being neutral or nearly so ($H_2N \rightleftharpoons OH$). This action cannot readily be ascribed to supplementary valencies, and not invariably to the existence of double bonds between the atoms. H. W.

Effect of an Electric Field on the [Spectrum] Lines of Argon and Oxygen. E. BÖTTCHER and F. TUCZEK (*Ann. Physik*, 1920, [iv], **61**, 107—112).—The effect of an electric field of 26,000 *V*/*cm* on the spectrum lines of argon, and on both the spark and arc lines of oxygen, has been investigated. In the case of argon, the lines are absolutely unaffected by the field; the same result was obtained with the spark lines of oxygen. Of the arc lines the 3—7 members of the I subsidiary triplet series showed a displacement towards the red which increased with increasing member number. The four lines λλ 4846, 4743, 4634, and 4559 are observed in the spectrum under the influence of the field, and have not before been observed. They are displaced toward the violet. The intensity increases with increasing wave-length, and the series ceases with the most intensive member without any indication of a further less intensive member. The *p*-components are considerably more intensive than the *s*-components. With increasing strength of field the intensity of the lines with longer wave-lengths increases more rapidly than that of those with shorter wave-lengths. The lines are regarded as belonging to a sharp subsidiary series of the I triplet subsidiary series. J. F. S.

Spectro-analytical Investigation of the Luminosity of Decomposing Ozone. KARL STUCHTEY (*Zeitsch. wiss. Photochem.*, 1920, **19**, 161—197).—The spectrum of the luminosity of an oxygen–nitrogen mixture in an ozoniser has been photographed and shown to be made up of the second positive group of the nitrogen spectrum, the emission spectrum of the *Y*-oxide of nitrogen (Warburg and Leithäuser, A., 1906, ii, 743; 1907, ii, 342; 1909, ii, 226, 227), and the visible emission spectrum of ozone. The emission spectra agree absolutely with the well-known absorption

spectra. On heating ozone at 400° in a specially constructed oven a strong luminosity is observed. The light shows both the visible and the ultra-violet spectra of ozone. A mixture of nitrogen and ozonised oxygen heated in the same furnace shows, in addition to the emission spectrum of ozone, also the emission spectrum of the γ-oxide of nitrogen. An explanation of the mechanism of the luminosity is given, and it is shown that the luminosity does not depend on presence of oxidisable substances. J. F. S

A Helium Series in the Extreme Ultra-violet. THEODORE LYMAN (*Nature*, 1919, **104**, 314; *Science*, 1919, **50**, 481—483).—By using a powerful disruptive discharge in helium a fairly strong line, in addition to those previously reported for the helium spectrum, was found to appear at wave-length 1640·2, and a fainter line at about 1215·1. Experimental evidence is thus afforded for the existence of the lines 1640·1 and 1214·9 as calculated from theoretical considerations. CHEMICAL ABSTRACTS.

Some New Spark Spectra in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, **170**, 320—322).—Using the spectrograph with a fluorspar prism, previously described (*ibid.*, 226), the authors have studied the spectra from a condensed spark between metallic electrodes in hydrogen in the case of four metals. Cadmium gave a spark spectrum extending to $\lambda=1500$, and the rays have been measured down to $\lambda=1600$. Bismuth gave a spectrum to $\lambda=1500$, the rays being measured to $\lambda=1550$. The spark spectrum of nickel is very rich in rays in the extreme ultra-violet, these being measured to $\lambda=1540$. Down to $\lambda=1650$ there is a great similarity between the arc and spark spectra. For silver the rays were measured down to $\lambda=1496$. Nickel gave a doublet, $\lambda=1550·7$ and 1548·2, and silver gave a doublet, $\lambda=1551·3$ and 1548·7. W. G.

Line Spectra of Cadmium and Zinc in the Electrodeless Ring Discharge. A. HAGENBACH and H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 129—142).—The spectra of zinc and cadmium produced from an electrodeless discharge have been measured and compared with the arc and spark spectra of these elements. It is shown that the spectrum coincides neither with the arc spectrum nor with the line spectrum in either case, but contains lines of both spark and arc spectra as well as a number of new lines. The intensity of the various lines is also very different from that of the lines in the arc and spark spectra. In the case of cadmium, lines are measured from λ 6467·4 to 2183·1, and forty-four new lines lying between λ 5511·0 and 2436·25 are recorded both in the international system and in Rowland's system. In the case of zinc, the lines measured lie between λ 6362·58 and 2252·87 and thirteen new lines lying between λ 3186·24 and 2246·88 are recorded. It is also shown that under suitable conditions a band spectrum can also be obtained. J. F. S.

Band Spectrum of Zinc from the Electrodeless Ring Discharge. A. HAGENBACH and H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 142—148. Compare preceding abstract).—The band spectrum of zinc obtained from an electrodeless discharge has been measured over the range λ 4894·9—3469·5, and compared with existing measurements. A large number of new bands are recorded. J. F. S.

Measurement of the Arc Spectrum of Iron below λ 2373 according to the International System. H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 149—158).—The iron spectrum of smaller wave-length than λ 2373 has been photographed and measured. The wave-lengths are given on the international system, and an accuracy of about 0·03 Å. is claimed for the values. As source of light an iron arc burning with 4 amperes and 220 volts was used. The values are compared with those of Kayser and Runge. J. F. S.

Theory of Absorption Spectra. I. LIFSCHITZ (*Schweiz. Chem. Zeit.*, 1918, **2**, 58; from *Chem. Zentr.*, 1919, iii, 970).—A reply to Kauffmann's criticisms (A., 1917, i, 391) of the author's views (A., 1917, ii, 435). H. W.

The Chromophore Function. V. Optical Properties of some Heavy Metal Complexes. I. LIFSCHITZ and ERNST ROSENBOHM (*Zeitsch. wiss. Photochem.*, 1920, **19**, 198—214. Compare A., 1917, ii, 62, 435).—The absorption spectra of the heavy metal complexes consist in general of at least three bands which lie between λ 6000 and λ 2000 Å. units. Of these, that with the longest wave-length depends mainly on the nature of the central atom; the next band depends on the nature of the co-ordinated groups if the central atom is the same. The band with shortest wave-length is not so completely investigated, because in many cases it lies so far in the ultra-violet as to be unmeasurable with the apparatus employed. All the work on the subject tends to show that this band is displaced more toward the longer wave-lengths in the presence of bivalent co-ordinated groups than in the presence of univalent groups. J. F. S.

Calculation of the Frequency Limits of Absorption K and L of the Heavy Elements. LOUIS DE BROGLIE (*Compt. rend.*, 1920, **170**, 585—587).—For tungsten, platinum, gold, lead, bismuth, thorium, and uranium examined, Vegard's formula gives results for the frequency limits of absorption, K and L, which are much more nearly in agreement with the mean of the observed results than those calculated by Bohr's formula. W. G.

Absorption Coefficients of Solutions for Monochromatic Radiation. E. O. HULBURT and J. F. HUTCHINSON (*Carnegie Inst. Pub.*, 1918, **260**, 6—69).—The absorption-coefficient of solutions of inorganic salts in water and in different alcohols has been

measured at intervals of 20 $\mu\mu$ to 40 $\mu\mu$ throughout the spectrum region from 600 $\mu\mu$ to 1300 $\mu\mu$. For each salt a series of solutions varying in concentration from saturation to moderate dilution was prepared, and the absorption curve drawn for each solution. The molecular absorption-coefficient, A, of the salt was calculated for each wave-length and plotted against c, the concentration of the salt in gram-molecules. Solutions of cobalt chloride in water, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols were examined by the photographic method; the values of A changed with the concentration, and the absorption curves for the higher alcohols were similar to those for ethyl alcohol. The following solutions were also examined: cobalt nitrate and sulphate, nickel chloride (anhydrous and the hexahydrate), nitrate and sulphate in methyl, ethyl, and propyl alcohols; ammonium ferric alum in water; chromic chloride, nitrate, and sulphate; and potassium permanganate. The relation between A and c has been determined from the data thus obtained. In general, A is not constant. Sometimes it decreases with dilution, in other cases increases with dilution, and also passes through a minimum; a maximum was not obtained. The deviations of A from a constant value were usually small, except at certain points in the spectrum, which in general were situated at the edges of absorption bands.

No theory adequately explains the observations.

CHEMICAL ABSTRACTS.

Colour Antagonism or Chemical and Electrical Polarity of the Spectrum. GABRIELE RABEL (*Zeitsch. wiss. Photochem.*, 1919, **19**, 69—128).—The long-wave half of the spectrum from the yellowish-green to the infra-red is termed positive light, whilst the short-wave half from bluish-green to ultra-violet is termed negative light. It is shown that phosphorescent light is produced by negative light and extinguished by positive light. Phosphorescent substances and certain classes of organic substances change their colour when subjected to negative light, but in positive light regain the original colour. Silver salts are reduced by negative light, but are oxidised by positive light. Certain biological and chemical reactions occur in the reverse direction in negative light from that in positive light. Electrodes which are sensitive to light undergo opposite potential changes in negative light from those in positive light. The retina of the eye belongs to the light sensitive electrodes. The movements of lower organisms are influenced in opposite ways by positive and negative light. In high-tension discharge in hydrogen, in the red hydrogen layers, the maximum potential lies in the luminous layer, the minimum in the dark space between the layers, whilst with the blue hydrogen layers the maximum is in the dark space and the minimum in the luminous layer. In the bluish-red double layers the dark space shows neither maximum nor minimum, but is positive to the blue layer and negative to the red layer. If a plate covered with sodium chloride is brought into a luminous layer discharge, reduction (that is, formation of a blue

coloration) occurs in the luminous layer in the blue discharge, and in the dark space in the red discharge. J. F. S.

Fluorescence and Absorption of the Uranyl Sulphates. E. L. NICHOLS and H. L. HOWES (*Physical Rev.*, 1919, [2], **14**, 293—305).—The fluorescence spectrum of the uranyl sulphates consists of eight equidistant bands, the first and eighth of which disappear at the temperature of liquid air. The remaining bands are resolved into groups of narrow line-like bands, the homologous members of which form series having constant frequency intervals, ranging from 85·7 in $UO_2SO_4,Cs_2SO_4,2H_2O$ to 83·0 in

$UO_2SO_4,K_2SO_4,2H_2O$.

The fluorescence groups are distinguished by a strong pair of bands about eight frequency units apart and several weak bands, some of which are doublets. There is a shift of all bands towards the violet, with increasing molecular weights, of about fifteen frequency units in passing from the spectrum of uranyl sulphate to that of the cæsium double salt. The absorption spectra of the sulphates are made up of series of bands having a frequency interval of 70·3 on an average. These absorption series extend into group 7 of the fluorescence without break of interval. There are many reversals where fluorescence and absorption overlap. The reversing region is, therefore, one group further towards the red than in most spectra of the uranyl compounds. CHEMICAL ABSTRACTS.

Fluorescence and Absorption of the Uranyl Acetates. E. L. NICHOLS, H. L. HOWES, and FRANCES G. WICK (*Physical Rev.*, 1919, [2], **14**, 201—221).—The paper deals with the fluorescence and absorption spectra of the two known forms of uranyl acetate and of thirteen double uranyl acetates as they appear when excited at the temperature of liquid air. The essential identity of the spectra of the double acetates of lithium, potassium, calcium, manganese, and strontium, both as regards the location of the principal bands and the structure of the fluorescence groups, is established and the deviations from this type occurring in the spectra of the uranyl acetates containing barium, ammonium, rubidium, sodium, magnesium, zinc, silver, and lead are considered. The approximate identity of frequency intervals for all series and for all salts is likewise established, the interval being 84·76.

CHEMICAL ABSTRACTS.

Quanten Theory Basis of Photochemistry. E. WARBURG (*Zeitsch. Elektrochem.*, 1920, **26**, 54—59).—A theoretical paper in which it is shown that every photochemical reaction is characterised by the specific photochemical action ϕ, that is, by the number of gram cals. of heat absorbed per mol. The fundamental law of photochemical reaction is, that energy of frequency ν is absorbed in quanta by the reacting molecules. The molecules which absorb the light radiation are termed "photochemical reserved molecules," and from the law stated, the number of these may be calculated. Valency radiation is the radiation which in the reserving

of 1 mol. of the photolyte is absorbed by it. The indicated photochemical equivalent (p) is the number of mols. which are reserved in the absorption of 1 gram-cal. The effective photochemical equivalent is the number of mols. which are decomposed or changed by the absorption of 1 gram-cal. It is equal to the specific photochemical action ϕ when this is calculated on the number of decomposed or changed molecules. ϕ/p is the efficiency relationship. Einstein's photochemical equivalent law says that every absorbing or reserved molecule is by the act of absorption decomposed or changed, and when the secondary processes are known it determines the efficiency relationship for which values $\gtreqless 1$ are obtained. The law is rigidly held in isolated cases only, because in general the reserved molecules, or at least a part of them, do not undergo primary change for the following reasons: (1) the valency radiation is smaller than the molecular decomposition energy; (2) energy is lost during the absorption of the radiation; and (3) the chemical change only takes place as a secondary process as in the case of photolytic isomerisation. J. F. S.

Photochemical Studies. VIII. Periodic Light Reactions. JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, **19**, 22—39). —The action of chlorine on α-cyanocinnamic acid in carbon tetrachloride solution under the influence of light of wavelength $\lambda=436\,\mu\mu$ has been investigated at 17°. It is shown that there is no formation of a chlorine additive compound, and that the nitrile concentration has no influence on the reaction, but chlorine is used up linearly with time, and its use is due to a hitherto unknown reaction between carbon tetrachloride and chlorine. The reaction between carbon tetrachloride and chlorine was therefore investigated. It is shown that the absorption of chlorine is linear both with blue light $\lambda=436\,\mu\mu$ and ultraviolet light $\lambda=366\,\mu\mu$. Using the whole of the light from a uviol lamp, a periodic change in the concentration of the chlorine is observed. Further experiments show that in light, pure carbon tetrachloride yields free chlorine. The reaction is discussed, and the possibility of periodic light reactions shown. Two types of such reactions are indicated: (1) Periodic light reactions are a necessary consequence of the stationary condition of photochemical processes, and must occur periodically so long as light of various wavelengths acts. (2) Periodic light reactions are the result of the combination of different opposing reactions, which are brought into existence by light of different wave-lengths, and are influenced by different catalysts, and consequently tend to an equilibrium condition. J. F. S.

Photochemical Studies. VII. Equilibria in Photochemical Addition of Bromine. JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, **19**, 1—21).—Reactions of the type

$$CR^1R^2{:}CR^3R^4 + Br_2 \rightleftharpoons CR^1R^2Br{\cdot}CR^3R^4Br$$

are reversible, and are of such a nature that the equilibrium position, in the dark as well as in the light, depends on the temperature,

concentration, nature of the solvent, intensity of light, and the nature of the radicles R^1, R^2, R^3, and R^4. The reaction between bromine and α-cyanocinnamic acid in light has been investigated: $CHPh:C(CN)\cdot CO_2H + Br_2 \rightleftarrows CHPhBr\cdot CBr(CN)\cdot CO_2H$. The reactions were carried out in carbon tetrachloride solution, using light of wave-length $\lambda = 436\,\mu\mu$ at $7°$. It is shown that bromine does not react as Br_2, but as 2Br, and the reaction taking place is proportional to the square of the absorbed light energy. The displacement of the equilibrium is proportional to the light intensity. The equilibrium formula for the reaction has the form

$$Q = J(1 - e^{-ip(b-y)^2(a-y)})/py,$$

where y is the equilibrium constant of the dibromide, p the thickness of the layer of solution, a the initial concentration of the nitrile, b the initial concentration of the bromine, i the normal light absorption constant of bromine (for $\lambda = 436\,\mu\mu$ it is 0·2156 per millimol. concentration), and J the light intensity. The temperature-coefficient of the dark reaction of the dibromide decomposition is determined from the corresponding equilibrium displacement and found to be 2·14. It is suggested that the extreme ultra-violet rays have the opposite action to the long waves on this reaction.

J. F. S.

Spectral Photoelectric Sensitivity of Silver Sulphide and several other Substances. W. W. Coblentz and H. Kohler (*Bull. Bur. Standards*, 1919, **15**, 231—249; *Sci. Paper*, 1919, No. **344**).—Data are given of the change in the electrical resistance of the sulphides of silver and bismuth when exposed to radiations from $0·6\,\mu$ in the visible spectrum to $3\,\mu$ in the infra-red. Galena, cylindrite, pyrites, and jamesonite did not show photoelectric sensitivity for the highest spectral radiation intensities available. The sulphides of silver and bismuth are sensitive from $0·6\,\mu$ to $1·8\,\mu$. The photoelectric response for silver sulphide becomes fatigued at the ordinary temperature. The change in resistance of the crystal when exposed to radiation is first negative and then positive, the resultant change being negative and approximately one-fifth of the original change. At $-158°$ this polarisation phenomenon disappears, and the response to radiation is the same as that of other substances, such as selenium or molybdenite. The sensitivity is greatly increased when the temperature is lowered to $-158°$. The sensitivity curve is quite symmetrical, and shows a maximum at $1·2\,\mu$. An increase in the intensity of the exciting radiation shifts the maximum towards the long wave-lengths.

A spectral photoelectric sensitivity curve of bismuthinite was obtained at $-166°$, maxima occurring at $0·64\,\mu$ and $1·08\,\mu$.

Chemical Abstracts.

Photo-oxidation of Organic Compounds by Chromates. Joh. Plotnikow (*Zeitsch. wiss. Photochem.*, 1919, **19**, 40—56).—The photo-oxidation of ethyl alcohol of various concentrations by ammonium chromate and ammonium dichromate in light of wave-

length $\lambda = 436\,\mu\mu$ has been studied at 20°. It is shown that the velocity constant may be calculated by means of a linear equation, and that it is proportional to the concentration of the alcohol. Increase in the salt concentration causes the reaction velocity to approach a maximum. The absorption constants of the salt solutions have been measured, and are found to be a function of the alcohol concentration and show a maximum. The dichromate follows Beer's Law, but the chromate does not. The absorption changes brought about by the alcohol do not affect the reaction velocity. The velocities of oxidation are the same with chromate as with dichromate. The temperature-coefficient of the reactions is 1·02. These reactions in general exhibit a perfectly normal photochemical behaviour. J. F. S.

Biochemical Action of Light. F. Schanz (*Pflüger's Archiv*, 1918, **170**, 646—676; from *Physiol. Abstr.*, 1918, **3**, 552).—Observations on the lens of the eye have shown that the effect of light is to render protein less soluble. Some authors have attributed this change to certain substances accompanying the protein. The presence of acetone in diabetes coupled with the frequent occurrence of lenticular opacity suggested a series of experiments in which equal amounts of a protein solution in a series of quartz tubes were treated with increasing amounts of acetone. Series 1 and 2 were placed in the sunshine, whilst series 3 was incubated in the dark at 38°. After four days the contents of the various tubes were equalised by appropriate additions of acetone, the only distinction being that in series 1 and 3 the added acetone had been previously treated with light, whereas in series 2 it had not. The amount of precipitation, after the addition of ammonium sulphate, sodium chloride, and acetic acid by the method previously described, was then noted in each case. The results showed that the change from a more to less soluble condition of the protein was due to the effect of light on the protein itself; the reaction was, however, increased by the presence of acetone. The amount of acetone breakdown (amount of gas formed) was tested after exposure to a quartz lamp of acetone (1) in ordinary glass (absence of shorter rays than $\lambda\,30\,\mu\mu$); (2) in quartz (absence of shorter rays than $\lambda\,200\,\mu\mu$); and (3) shaded with a "euphos" glass screen (rays shorter than $\lambda\,400\,\mu\mu$). The results showed that acetone absorbed and was acted on by the ultra-violet rays alone. The author maintains that chemically pure organic salts are quickly broken down by the action of light in the absence of iron. Some quartz spectrographs figured in the text show absorption of the violet rays by protein and other substances, the greatest absorption being exhibited by acetaldehyde and acetone. Certain coloured substances, such as eosin, hæmatoporphyrin, and chlorophyll, act as optical sensitisers; eosin is non-toxic unless the organism is exposed to intense light. Mice die suddenly if exposed to daylight after previous injection of hæmatoporphyrin, and various lesions of the skin occur in sub-acute cases. It is suggested that the brilliant

colourings of flowers, etc., is to enable the organism to select the particular light rays required. Other experiments show that the growth of plants is affected by ultra-violet rays. J. C. D.

The Reaction of Proteins to Light. F. SCHANZ (*Pflüger's Archiv*, 1917, **169**, 82—86; from *Physiol. Abstr.*, 1917, **2**, 584).—The author refers to his previous work on the lens proteins, and also to Neuberg's work. Proteins are more sensitive to light than Neuberg considers, and experiments are given which show that quartz lamp rays can effect in them changes in solubility, etc., so that albumins then show the characters of globulins. J. C. D.

Some Observations on the Action of Coal on a Photographic Plate. ERIC SINKINSON (T., 1920, **117**, 165—170).

Chemical Actions of Radiation. EUGÈNE WOURTZEL (*Le Radium*, 1919, **11**, 289—298, 332—347. Compare A., 1914, ii, 18, 238).—The chemical action of α-rays from radium emanation on hydrogen sulphide, ammonia, nitrous oxide, and carbon dioxide has been investigated. When the reaction is not accompanied by secondary reactions, it is found that the amount of decomposition, under the same conditions of volume, pressure, and temperature, is proportional to the amount of emanation present. This is the case with the reactions $H_2S=H_2+S$ and $NH_3=N+3H$. The effect increases with the dimensions of the vessel, and the volume, but tends to a maximum value, corresponding with the total utilisation of the energy of the radiation. If K, K_∞ are the velocity constants for particular conditions and for total utilisation of energy respectively, R is the radius of the vessel, and p the pressure, then, when $K>0{\cdot}5K_\infty$, it is found that $K=K_\infty(1-C/Rp)$, where C is a constant. When $K<0{\cdot}5K_\infty$, the relation is represented by a line tangent to the above curve, and passing through the origin. The decomposition of nitrous oxide is complicated by a secondary reaction, namely, the formation of nitric peroxide from the nitric oxide and oxygen set free in the initial reactions $N_2O=N_2+O$; $N_2O=NO+N$. Contrary to the statement of Ramsay and Cameron, carbon dioxide is only very slowly decomposed by α-rays. No theoretical conclusions are drawn from the results beyond the statement that the decompositions do not follow Faraday's law. A full account of the apparatus used is given. J. R. P.

New Arrangement for the Röntgen [Ray] Crystallographic Investigation of Crystalline Powders. HELGE BOHLIN (*Ann. Physik*, 1920, [iv], **61**, 421—439).—A new arrangement is described, in which by means of a cylindrical arc-shaped scattering surface, made of a compressed, crystalline powder, interference lines can be produced. One edge of the lines is sharp and may be geometrically defined, whereby an increased accuracy over that of the previously described methods is rendered possible. It is shown that the sharpness and the position of the line edge is in-

dependent of the width of the slit and of the depth to which the radiation penetrates. By means of photographs of the interference lines the space grating of thorium, nickel, and magnesium has been determined by this method. It is shown that thorium and nickel have face-centred cubic lattices, whilst magnesium has a lattice made up of two simple interpenetrating hexagonal lattices. J. F. S.

An Experimental Determination of the Critical Electron Velocities for the Production of the Ionisation and Radiation on Collision with Argon Atoms. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 1—23. Compare A., 1919, ii, 210).—In the conclusion of Franck and Hertz that ionisation occurred in argon when the velocity of the colliding electrons was raised to 12 volts, the ionisation of the gas could not be distinguished from photoelectric effects of radiation produced by the collisions. By methods similar to those previously employed for helium, it has been shown that, when electrons bombard argon atoms, a radiation is produced when the electrons attain a velocity corresponding with 11·5 volts, which is not accompanied by ionisation of the argon, but at 15·1 volts ionisation of the argon takes place. The latter potential corresponds, according to the quantum relation, with a wave-length of 817 Å.U., which is in accord with the spectroscopic investigation of the extreme ultraviolet spectrum of argon by Lyman, which he found terminated abruptly at 800° Å.U. Evidence has been obtained that at 15·1 volts not all the collisions are fruitful in producing ionisation, and that the fraction of fruitful collisions is increased greatly by intense 11·5 volt radiation. The minimum ionisation velocity, 15·1 volts, however, is the same whether the argon is exposed to weak or intense 11·5 volt radiation. F. S.

Investigation of the Effects of Electron Collisions with Platinum and with Hydrogen, to ascertain whether the Production of Ionisation from Platinum is due to Occluded Hydrogen. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 23—43).—During the investigation of electron collisions with helium it was found that positive ions were produced from a positively charged platinum gauze bombarded with electrons of minimum velocity corresponding with 11 volts, and this has been more fully investigated to determine whether it is due to the metal or to attached hydrogen. This voltage is subject to a correction for the velocity at which the electrons leave the tungsten filament, and the mean of all the corrected results gives 13·0 volts as the critical electron velocity for the production of the ionisation, which does not agree with the usually accepted value of the "ionisation potential" of hydrogen (11 volts). In the same apparatus the production of ionisation in hydrogen was investigated, hydrogen being introduced through a palladium tube heated in a flame, and the conclusion was reached that the first critical velocity (13 volts) is not due to hydrogen at all, but probably

to the platinum itself. In hydrogen it was found that a radiation is produced at an electron velocity of 10·5 volts, a second type of radiation at 13·9 volts, an ionisation at 14·4 volts, and a second type of ionisation at 16·9 volts. These four velocities correspond probably with radiation from the hydrogen atom and molecule and ionisation of the hydrogen atom and molecule respectively, the values calculated from Bohr's theory being 10·2 instead of 10·5 for the first, 13·6 instead of 14·4 for the third, and 16·3 instead of 16·9 for the fourth. It is desirable that these critical velocities be further examined in an apparatus specially designed for the purpose. F. S.

Melting Point of Lead Isotopes. M. E. LEMBERT (*Zeitsch. Elektrochem.*, 1920, **26**, 59—60).—The melting points of pure lead chloride and lead chloride containing Ra-*G* chloride have been determined and shown to agree to within 0·06%, that is, to within 0·5°. The material used for the determination was that used by Richards and Lembert for atomic-weight determinations, and from which the values 207·15 and 206·57 respectively were obtained (A., 1914, ii, 683). The present results confirm the assumption of Fajans (A., 1915, ii, 206) that ν^2m is constant for isotopes as against the view of Lindemann (*Nature*, 1915, **95**, 7) that ν is constant. J. F. S.

The Radioactivity of Bavarian Rocks and Waters and of the Fluorspar of Wölsenberg. F. HENRICH (*Zeitsch. angew. Chem.*, 1920, **33**, 5—8, 13—14, 20—22).—An investigation of the distribution of radioactivity in the springs, rocks, and minerals of Bavaria, including also French Switzerland, the Fichtelgebirge, and the Oberpfalz, is described with details of the activity of a large number of springs expressed in Mache units (*M.U.*). The springs in the chalk mountains of French Switzerland were but feebly active, but in the granitic areas of the Fichtelgebirge most of the springs had an activity between 10 and 100 *M.U.* and four were over 100 *M.U.* The minerals tobernite and autunite occurred in these districts in the granite. A special examination of the gases from one of the springs showed the unusual composition of about 12% of oxygen and the rest "unabsorbable."

A description is given of the fluorspar of Wölsenberg ("Stinkfluss"), in which the dark blue and violet-coloured varieties emit a peculiar odour on being crushed, which is undoubtedly due to the evolution of free fluorine. The origin of this is considered to be due to the action of rays of radioactive substances, dissociating the calcium fluoride, with coloration of the mineral due to colloidal calcium and evolution of free fluorine. By acting on fluorspar with radium rays the colour is easily produced, but not the odour of fluorine. F. S.

Dependence of the Dielectric Constants of Water, Ethyl Alcohol, Methyl Alcohol, and Acetone on Pressure. G. FALCKENBERG (*Ann. Physik*, 1920, [iv], **61**, 145—166).—The dielec-

tric constant of water, ethyl alcohol, methyl alcohol, and acetone has been determined at temperatures (16·3—20°) over the pressure range 7—200 atms. The mean change in the dielectric constant per atmosphere increase in pressure is found to be 0·0046% for water, 0·0097% for ethyl alcohol, 0·0102% for methyl alcohol, and 0·016% for acetone. The refraction constants $(n-1)/d$, $(n^2-1)/d$, and $(n^2-1)/(n^2+2) \cdot 1/d$ are calculated for the above-named liquids at the pressures named. In the case of water and both alcohols a good agreement is found for the expression $(n^2-1)/d$, both at low and high pressures. In the case of acetone, owing to insufficient knowledge of the compressibility, conclusions are not arrived at. Using the results of Ortvay (A., 1911, ii, 961), the values of $(n^2-1)/d$ and $(n-1)/d$ are calculated for benzene and ethyl alcohol. In the case of benzene the value of $(n^2-1)/d$ is constant over the range 1—500 atmospheres: but with ethyl alcohol all three values show considerable irregularity over the same pressure range. The very large values of the Wiener number u for water and the two alcohols confirm the suggestion of Röntgen that the ratio of polymerised to non-polymerised molecules changes with increase of pressure. J. F. S.

[Electrical] Conductivity of Solid Salts and Mixtures of Salts. ROBERT KETZER (*Zeitsch. Elektrochem.*, 1920, **26**, 77—84). —The specific conductivity of pastilles of lead chloride, lead bromide, and mixtures of these substances with varying amounts of sodium and potassium chloride and bromide respectively has been determined at 37°. Electrical contacts were made with amalgamated copper plates, and it is shown that differences in conductivity amounting to 12% may be occasioned by variations in the pressure employed in making the pastille. It is shown that the large increase in conductivity found by Fritsch (A., 1897, ii, 301) on mixing the haloids of lead and mercury with alkali haloids, does not occur if moisture is completely removed and if the mixture is not heated to a high temperature. It is shown that the previous treatment of lead chloride has a marked influence on the conductivity. In the case of the mixtures, it is found that heating before pressing increases the conductivity to a considerable extent. Thus 2% of sodium chloride in lead chloride increases the conductivity of the lead chloride 109—170 times, if the previous heating was carried out in moist air, in a vacuum, or in chlorine; on heating in dry air the increase was 41 times. The very smallest additions to lead chloride produced a considerable increase in conductivity; thus, 0·001% of sodium chloride increased the conductivity 45 times if the mixture was melted in chlorine before pressing. No proportionality was found between the concentration of the alkali chloride and the increase in conductivity. J. F. S.

Form of the Conductivity Function in Dilute Solutions. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1—18).—A theoretical paper, in which the method adopted by Washburn (A., 1918, ii, 55) for calculation of the value of k_0 is examined

The author is not able to agree either with Washburn's conclusions or with his interpretation as to the limiting character of the law of mass action. J. F. S.

Conductivity and Viscosity of Organic and Inorganic Salts in Formamide and in Mixtures of Formamide with Ethyl Alcohol. P. B. Davis and H. I. Johnson (*Carnegie Inst. Pub.*, 1918, **260**, 71—96).—The conductivity and the viscosity in formamide solution of (*a*) metallic nitrates and formates (common anion), and (*b*) sodium salts of organic acids (common cation) have been measured, and also the behaviour of certain representative salts in mixtures of formamide and ethyl alcohol has been studied. The molecular conductivities of ammonium, potassium, sodium, calcium, strontium, and barium nitrates in formamide, which has a greater dissociating power than water, are much smaller than in aqueous solution. Evidence of complex solvent formation is obtained with the calcium, strontium, and barium salts in formamide and in water. From the conductivities and viscosities of the formates of rubidium, ammonium, lithium, sodium, barium, and strontium in formamide at 15°, 25°, and 35°, the conclusions are drawn that these salts, like the nitrates, are more strongly dissociated at low dilutions in formamide than in water, that the temperature-coefficients of the conductivities are of the same order of magnitude for the alkali formates, but are greater for the alkaline-earth formates, and that rubidium and ammonium formates increase the viscosity less than sodium and lithium formates.

From conductivity and viscosity measurements in formamide at 15°, 25°, and 35° of sodium *m*-bromo-, *m*-amino-, and 3 : 5-dinitrobenzoate, benzoate, salicylate, benzenesulphonate, and succinate, the conclusions are drawn that (*a*) the conducting capacity of the first three salts is approximately the same, and the same is true of the next three. All monobasic salts have nearly the same conductance, which is about half that of the dibasic salt; (*b*) no relation exists between the conductivity and the constitution of the organic salts, and the same is true of the viscosity.

Data were also obtained on the molecular conductivity and the viscosity of tetramethylammonium iodide, rubidium iodide, lithium nitrate, and calcium nitrate in mixtures of formamide and ethyl alcohol. The first three salts show an increase in molecular conductivity up to a concentration of 25% formamide and 75% ethyl alcohol, where a maximum is reached, a fact explicable by an increase of ionic mobility at this point. Cæsium, rubidium, and potassium salts lower the viscosity of water, but increase that of formamide. Chemical Abstracts.

Electrical Conductivity of the Sodium Salts of certain Organic Acids in Absolute Alcohol at 15°, 25°, and 35°. H. H. Lloyd and A. M. Pardee (*Carnegie Inst. Pub.*, 1918, **260**, 99—118).—An extension of previous work on the electrical conductivity and dissociation of various organic acids in alcoholic solu-

tion, involving a study of the sodium salts of the organic acids in absolute alcoholic solution to obtain first the λ_0 values for these salts and then the λ_0 values for the acids. Absolute alcoholic solutions of thirty-two sodium salts were prepared, and the conductivities at 15°, 25°, and 35° over the range $N/50$ to $N/20,000$ were determined. Goldschmidt's previous results were confirmed. The λ_0 values were obtained by extrapolation, using the function $1/\lambda = 1/\lambda_0 + K(C\lambda)^{n-1}$ developed by Noyes and Johnston. The Kohlrausch formula did not give satisfactory results. The λ_0 values at 25° were obtained for all the salts, and by combination with the λ_0 values for hydrogen and sodium chlorides the limiting conductivity at 25° of thirty-one organic acids in absolute alcoholic solution was calculated. The dissociation and affinity constants of these acids in such solution can be calculated from the λ_0 values. There is a great similarity in the conductivity of these organic acids in alcohol. Little can be said of the relation between chemical composition and conductivity. No difference was found between aliphatic and aromatic derivatives, and the position of substituents in the latter appeared to be without influence on the conductivity. CHEMICAL ABSTRACTS.

The Positive Influence which the $\alpha\gamma$-Diols Exercise on the Conductivity of Boric Acid. J. BÖESEKEN (*Rec. trav. chim.*, 1920, **39**, 178—182).—[With W. ROST VAN TONNINGEN.]—Diethylmalonic acid has $K_{25} = 2 \cdot 8 \times 10^{-3}$, and is notably much stronger than diglycollic acid (compare A., 1916, ii, 595). It might be expected, therefore, to have a feebler negative influence on the conductivity of boric acid, but the diminution found is almost the same in the two cases.

[With W. F. Th. HENDRIKSZ.]—Measurements with β-nitro-β-methylpropane-$\alpha\gamma$-diol give results almost equal to those of glycerol and much less than those of pentaerythritol. W. G.

The *cyclo*Hexane-1 : 2-diols and the Flexibility of the Benzene Ring. J. BÖESEKEN and J. VAN GIFFEN (*Rec. trav. chim.*, 1920, **39**, 183—186).—Measurements have been made with the *cis*- and *trans*-*cyclo*hexane-1 : 2-diols to determine their influence on the conductivity of boric acid. The influence of both isomerides is manifestly negative, but the influence of the *cis*-isomeride is slightly more feeble than that of the *trans*-isomeride. The *cis*-diol shows a greater tendency to form complexes than the *trans*-diol. The authors explain the difference of behaviour of these two isomerides on the hypothesis that the flexibility of the *cyclo*hexane ring permits of the hydroxyl groups of the *cis*-form obeying more easily their natural repulsion. W. G.

Increase in the Conductivity of the α-Keto-acids by Boric Acid, as a Consequence of the Formation of α-Hydroxy-acids by Hydration: $R \cdot C(OH)_2 \cdot CO_2H$. J. BÖESEKEN and W. ROST VAN TONNINGEN (*Rec. trav. chim.*, 1920, **39**, 187—190).—Trimethylpyruvic acid, like pyruvic acid itself (compare A., 1916,

ii, 209), exerts a marked positive influence on the conductivity of boric acid itself, thus confirming the view previously expressed (*loc. cit.*) that the α-keto-acids in aqueous solutions are hydrated and behave like dihydroxy-compounds. Trimethylpyruvic acid is notably much weaker than pyruvic acid, and the dehydration takes place more easily, so that it apparently exerts a negative influence even at moderate dilutions. W. G.

Overpotential and Catalytic Activity. ERIC K. RIDEAL (*J. Amer. Chem. Soc.*, 1920, **42**, 94—105).—The influence of temperature on overpotential has been determined at a series of temperatures for platinum, copper, and zinc. In the case of zinc, there is no relationship between the calculated and observed temperature-coefficient, the latter only amounting to 0·31 millivolt per degree at 37°. In the case of copper and platinum, a higher coefficient is observed, the values being 2·2 millivolts per degree and 0·17 millivolt per degree respectively. These values are three to four times as large as the calculated values. It is suggested that overpotential is a measure of the energy required for the desorption of hydrogen from a metal surface. Metals with low latent heats of desorption are catalytically active, the activity increasing with decreasing overpotentials. Metals with overpotentials exceeding 0·455 volt are catalytically inert, and no metal can posess an overvoltage exceeding 1·80 volts. The calculated values of the catalytic activities of the metals are in agreement with Sabatier's qualitative observations. A suggestion is made for the mechanism of the process of desorption on the radiation hypothesis. J. F. S.

Resemblances between the Properties of Surface Films in Passive Metals and in Living Protoplasm. II. RALPH S. LILLIE (*Science*, 1919, **50**, 416—421. Compare A., 1919, i, 606). —Most ions activate passive iron at varying rates and the stability of the surface film in any solution, and hence the preservation of the passive state, is dependent on the oxidising properties of the dissolved substance. Continued oxidation seems to be necessary for preservation of passivity. Ions of strong oxidising properties tend to stabilise regardless of charge, for example, the dichromate, permanganate, silver, gold, and platinum ions. The haloid ions have a strong activating influence, the rate being proportional to the concentration. Salts with terminal oxygen in union activate only very slowly. The cation has not so large an effect, but passivity is retained longer in solutions of heavy metal salts. Any condition that confers increased stability on the surface film prevents or retards its destruction in an activating solution. Hence oxidising anions or cations more noble than the experimental metal antagonise the activating effects of other ions. The antagonism between sodium and calcium so characteristic in biological systems is not exhibited by passive iron. Anæsthetics, except ethyl nitrate, show no retarding effect towards activation as they do in protoplasm, but

this is not to be expected since solution in the organic solvents of the protoplasm, particularly lipoids, is not paralleled by any process of solution in the metals. CHEMICAL ABSTRACTS.

Simple Hydrogen Electrode. C. H. BAILEY (*J. Amer. Chem. Soc.*, 1920, **42**, 45—48).—The vessel and electrode for preparing a simple hydrogen cell may be constructed as follows. A piece of 7 mm. bore tube is blown out at one end to form a bulb 15 mm. diam.; the tube is then bent to form an angle of about 45° at a distance of 50 mm. from the top of the bulb. The other limb of the tube is about 80 mm. long, and is fitted with a ground-glass stopper. The metal electrode is a thin gold disk 5 mm. diam. welded to a piece of thin platinum wire and fused into the side of the shorter limb of the tube about 5 mm. above the bend. The gold foil is platinised in the usual way. The tube is filled with the liquid under investigation, and then by means of a fine tube the bulb is filled with pure hydrogen, thus expelling some of the liquid. It is then stoppered, care being taken to exclude all air, and vigorously shaken until the solution is saturated with hydrogen. Connexion is made with the standard electrode by removing the stopper and placing the syphon tube well down the longer limb. The electrode is stated to give trustworthy results, and to be very rapid in its action. J. F. S.

A Gas Collecting Tube. ERICH MÜLLER (*Zeitsch. Elektrochem.*, 1920, **26**, 76—77).—A gas burette for collecting the gases evolved at electrodes during electrolysis is described. The novelty of the apparatus lies in the tap which is attached at the bottom of the burette; this is a heavy tap with a key bored in T-shape, so that the horizontal bore will give access to the burette and the vertical bore to a side-tube to which the levelling tube is attached.

J. F. S.

New Cadmium Vapour Arc Lamp. FREDERICK BATES (*Phil. Mag.*, 1920, [vi], **39**, 353—358).—A small quartz cadmium vapour lamp is described. The lamp is in the form of an inverted U-tube of 10 c.c. capacity, and is fitted with two long quartz capillaries at its ends, by means of which the tungsten wire electrodes are admitted. The electrodes are fastened into the capillaries by means of lead seals. The lamp is filled by distilling, from a quartz bulb attached at the bend of the U-tube, a gallium–cadmium alloy containing 2—3% of gallium. The presence of the gallium renders the cadmium soft, and so prevents breakage of the lamp when the metal solidifies. The distillation is carried out at 0·001 mm. pressure, and when sufficient has been distilled into the lamp the narrow tube by which the bulb is connected is sealed. The lamp will burn with 110 volts and 3 amperes with a drop of 14 volts across the terminals, but is more efficient with a current of 7 amperes and a drop of 25 volts. To start the lamp one limb must be heated with a bunsen flame. The spectrum of the light thus produced is prac-

tically that of pure cadmium; the lamp is durable, and requires little attention, and furnishes an intense monochromatic source of red light by means of the line λ 6439 Å. J. F. S.

Magnetic Susceptibilities of Hydrogen and some other Gases. TAKÉ SONÉ (*Phil. Mag.*, 1920, [vi], **39**, 305—350, and *Sci. Rep. Tohoku. Imp. Univ.*, 1919, **8**, 115—167).—The magnetic susceptibility of air, oxygen, carbon dioxide, atmospheric nitrogen, chemically pure nitrogen, argon, and hydrogen has been determined with reference to water $= -0.720 \times 10^{-6}$. The following specific susceptibilities ($\chi\,10^6$) at 20°, and volume susceptibilities ($\kappa\,.\,10^6$) at 0° and 760 mm. are found: air, $\chi = 23.85$, $\kappa = 0.03084$; oxygen, $\chi = 104.1$, $\kappa = 0.1488$; carbon dioxide, $\chi = -0.423$, $\kappa = -0.000836$; chemically pure nitrogen, $\chi = -0.265$, $\kappa = -0.000331$; atmospheric nitrogen, $\chi = -0.360$, $\kappa = -0.000452$; argon, $\chi = -5.86$, $\kappa = 0.0104$; hydrogen, $\chi = -1.982$, $\kappa = -0.0001781$. The susceptibility of air as determined is very close to that calculated from the values for the constituent gases, which indicates that the additive rule holds for the susceptibility of gases. The susceptibility of nitrogen is found to be diamagnetic, a fact which is opposed to the values of all other observers except Pascal, who found it had a value about 50% greater than the present value. The specific susceptibilities of gaseous and solid carbon dioxide have the same value. The present results are considered in the light of Bohr's atomic model for hydrogen. J. F. S.

Moment of Inertia of the Magneton. R. GANS (*Ann. Physik*, 1920, [iv], **61**, 396—397).—A theoretical paper, in which the moment of inertia of the magneton of a number of elements is calculated. This value is of the same order in most cases, and lies between 0.761×10^{-43} and 60.2×10^{-43}. The moment of inertia of platinum is 67.7×10^{-40} and of anhydrous manganous sulphate 12.4×10^{-40}. J. F. S.

Magneto-chemistry of the Chromic Chlorides. JOSÉ BALTÁ ELIAS (*Anal. Fis. Quim.*, 1918, **16**, 467—483).—The magnetic susceptibility of aqueous solutions of the green and the violet chromic chloride was determined at different degrees of concentration, temperature and acidity, and during transformation of either modification into the other. Quincke's method was employed for dilute, and the solenoid method for concentrated, solutions. The susceptibility of the solutions of either salt was found to be independent of the concentration, hence they comply with Wiedemann's law (that is, the susceptibility is an additive property, obtained as the sum of those of its components). The conversion of the green into the violet solution and vice versa was not marked by any change in the magnetic constant within the intervals in which the measurements were made (up to eight hundred and eighty-six hours). Hence the two modifications have the same magnetic constant, whereas their

other physical properties are different. It is inferred that—unlike cobalt, the magnetic properties of which undergo profound changes in certain co-ordination compounds—the linking between chromium and the other atoms or radicles in its co-ordination sphere is effected through the more external electronic orbits of the atom. The existence of nineteen magnetons in the chromium atom is confirmed (compare Cabrera and Marquina, A., 1917, ii, 355). The magnetic constant of both salts decreases in dilute solutions, but in presence of hydrochloric acid hydrolysis is repressed and the (stable) green chloride regenerated. The figures obtained for the molecular susceptibilities ($\chi^{(M)}$) of the two compounds are given below, together with those obtained by Feytis (A., 1913, ii, 381):

	Elias.	Feytis.
$[Cr(H_2O)_6]Cl_3$	6181.10^{-6}	5920.10^{-6}
$[CrCl_2(H_2O)_4]Cl,2H_2O$ ...	6179.10^{-6}	6100.10^{-6}

W. R. S.

Establishing of the Absolute Temperature Scale. FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1920, **42**, 54—59).—A theoretical paper, in which the work of Buckingham and of Chappuis on the absolute temperature scale is considered from the point of view of the author's new equation of state, which is based on the Bohr conception of the atom (*Proc. Nat. Acad. Sci.*, 1917, 3, 323). J. F. S.

Characteristics of the Gouy Thermo-regulator. T. S. SLIGH, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 60—68).—The paper describes a modification of the usual type of electrical thermo-regulator in which the fixed contact element is replaced by an oscillating contact element, and shows that such a regulator will reduce the periodic variations of the bath temperature and the erratic variations due to variations of the mercury surface to a fraction of the values obtainable with the usual form of thermo-regulator. A periodic variation in bath temperature of less than 0·0001°, as indicated by a temperature indicator, having a natural period of about five seconds is easily obtained. By the use of an oscillating contact regulator, variations of mean bath temperature due to variations in external conditions are reduced below the values usually obtained. Characteristic equations are derived for both the fixed and oscillating type of thermo-regulator, and these equations, together with experimental data, have been used to draw a comparison between the two types of regulator. J. F. S.

Variation of Thermal Conductivity during the Fusion of Metals. SEIBEI KONNO (*Sci. Rep. Tohoku. Imp. Univ.*, 1919, **8**, 169—179).—The thermal conductivity has been determined for tin (18—498°), lead (18—601°), bismuth (18—584°), zinc (18—578°), aluminium (18—800°), and antimony (0—692°). The thermal conductivity of tin, lead, zinc, and aluminium decreases with rise of temperature up to the melting point. On melting the thermal

conductivity of these metals decreases abruptly and to a considerable extent. The thermal conductivity of bismuth and antimony decreases to a minimum, which lies at 160° and 182° respectively, and then slowly rises to the melting point. On melting the thermal conductivity of bismuth increases considerably, whilst that of antimony appears to decrease slightly. The thermal conductivity of the molten metals in all cases decreases slightly with increase in temperature. The changes in thermal conductivity run parallel with the changes in electrical conductivity with rise in temperature.
J. F. S.

Variation of Atomic Heats as a Function of the Temperature. MATHEUS D'A. ALBUQUERQUE (Pamphlet [Portuguese], 1919, 1—19).—A theoretical discussion.

Melting Points of Pure Metals. W. GUERTLER and M. PIRANI (*Zeitsch. Metallkunde*, **11**, 1—7; from *Chem. Zentr.*, 1919, iii, 910—911).—The following are given as the most trustworthy figures for the melting points of the elements: Ag, 961°; Al, 658°; As, 850° (?); Au, 1063°; B, 2400°; Ba, 850°; Gl, 1300° (?); Bi, 270°; C, >3600°; Ca, 809°; Cd, 321°; Ce, 700°; Cl, −101·5°; Co, 1490°; Cr, 1520°; Cs, 26°; Cu, 1084°; Fe, 1530°; F, −223°; Ga, 30°; Ge, 958°; H, −259°; Hg, −39·7°; I, 113·5°; In, 155°; Ir, 2350°; K, 62·4°; La, 810°; Li, 186°; Mg, 651°; Mn, 1210°; Mo, 2410° (?); N, −210°; Na, 97·5°; Cb, 1700° (?); Nd, 840°; Ni, 1452°; O, −218°; Os, 2700° (?); P, 930°; Pb, 327·4°; Pd, 1545°; Pr, 940° (?); Pt, 1760°; Ra, 700°; Rb, 38°; Rh, 1960°; Ru, 2450° (?); S, 119·2°; Sa, 1300°; Sb, 630°; Se, 217°; Si, 1420°; Sr<Ca<Ba; Sn, 232°; Ta, 2800°; Te, 450°; Th>Pt, 1800°; Ti, 2000° (?); Tl, 301°; U, >1850°; V, 1800°; W, 3030°; Y, 1490°; Zn, 419·4°; Zr, 1700° (?).

The dependence of the melting point on the position of the element in the periodic system is also graphically illustrated.
H. W.

Thickness of the Capillary Layer between the Homogeneous Liquid and Vapour Phases, particularly for Carbon Dioxide. G. BAKKER (*Ann. Physik*, 1920, [iv], **61**, 273—302. Compare A., 1919, ii, 12; this vol., ii, 19).—A theoretical paper, in which the thermodynamic equation $(E_1-E_2)/2-E_3=T^2\{d(H/\zeta T)/dt\}$ is deduced by two methods: H is the surface tension, ζ the thickness of the capillary layer, T the absolute temperature, and E_1, E_2, and E_3 are the energy densities (energy per unit volume) of the liquid, vapour, and unstable phases respectively. The thermodynamic potential of the unstable phase has the same value as the homogeneous liquid and vapour phases. Making use of the formulæ of Gauss—van der Waals and Mills, the following thicknesses are calculated for the capillary layer of carbon dioxide: −25°, 1·52 $\mu\mu$; −10°, 1·51 $\mu\mu$; 0°, 1·87 $\mu\mu$; 10°, 2·13 $\mu\mu$; 20°, 3·11 $\mu\mu$; 28°, 5·86 $\mu\mu$; 30°, 13·66 $\mu\mu$; and 31·12°, 193 $\mu\mu$. Mak-

ing use of a different method of calculation, the values for the number of layers in the capillary layer R and the total number of layers n of gas and liquid which form the capillary layer are calculated. For carbon dioxide the values are:

t =	−25°,	−10°,	0°,	10°,	20°,	28°.
R =	3·0	3·6	4·2	5·1	7·0	11·4
n =	2·7	3·4	4·0	4·9	6·9	11·3
ζ =	1·6	2·0	2·3	2·8	3·2	6·1 $\mu\mu$.

The value of R has also been calculated for benzene and ether. These are based on the van der Waals's equation of state, and are as follows: (1) benzene, 5·4°, 2·4; 50°, 3; 100°, 3·4; 150°, 3·5; 200°, 4·0; 250°, 10·8; and 280°, 16; (2) ether, 0°, 2·4; 20°, 3·3; 50°, 3·3; 80°, 4·2; 120°, 5; 170°, 7·8; 190°, 16·4; and 193°, 21·5. J. F. S.

Certain Binary and Ternary Mixtures of Liquids having Constant Boiling Points. WILLIAM RINGROSE GELSTON ATKINS (T., 1920, **117**, 218—220).

Brown's Formula for Distillation. SYDNEY YOUNG (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **15**, 667—672).—Brown's formula, $M'_A/M'_B = c \cdot M_A/M_B$ (where M'_A, M'_B, and M_A, M_B are the relative number of molecules of A and B in the vapour and liquid phase respectively, and c is a constant depending on the relative vapour pressures of the pure substances at the boiling point of the mixture), is applicable without serious error to mixtures of benzene and toluene, of which the vapour pressure P approximately equals $MP_A + (1 - M)P_B$, P_A and P_B being the vapour pressures of the two pure substances at the same temperature, and M the molar fraction of the substance A. Further, for benzene and toluene the best value of the constant c differs but slightly from the ratio P_A/P_B, namely, 2·591. G. F. M.

Thermodynamics and Probability. A. BERTHOUD (*J. Chim. Phys.*, 1919, **17**, 589—624).—A mathematical discussion of the relationship between entropy and probability, in which a formula is given by means of which it is possible (1) to determine the most probable distribution of the molecules of a monatomic or diatomic gas, according to their velocity or energy, this distribution being expressed by the generalised Maxwell formula; (2) to find the relationship which expresses the entropy of a monatomic or diatomic gas in terms of its temperature and its volume, this relationship agreeing with the thermodynamic expression of entropy. W. G.

Free Energy and the Hypothesis of Nernst. A. BOUTARIC (*Le Radium*, 1919, **11**, 257—262, 298—305, 348—356).—The author directs attention to the well-known looseness of terminology of writers on the free energy equation, $A - U = T(dA/dT)$. He deduces

this, and numerous other equations, by familiar methods, and considers their application to some special examples. J. R. P.

Heats of Dilution of Certain Aqueous Salt Solutions. Allen Edwin Stearn and G. McP. Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 18—32).—The reversible molecular heat of dilution has been determined for the chlorides of sodium, potassium, and strontium at various concentrations ranging from 3·2 weight N to 0·2 weight N, and also for solutions of mixtures of pairs of the above-named salts in equivalent and molecular quantities. The heats of dilution of sodium and potassium chlorides are negative. This fact in the light of the equation $L_{U}=RT^2.(d\log_e p/p_0)/dT$, in which L_U is the molecular heat of dilution, indicates an increase in the degree of ionisation with temperature, which is contrary to the experimental results of Noyes (A., 1912, ii, 526), unless they are explained on the basis of decomposition of complexes which exist in solution, but are decomposed on dilution. The heats of dilution for the solutions of mixed salts bear no simple additive relation to the heat effects of the single components at equivalent concentrations. The results are explained on the basis of higher order compounds as put forward by Werner. J. F. S.

Heats of Dilution of Solutions of Barium Chloride and Barium-Sodium Chloride Mixture. G. McP. Smith, Allen E. Stearn, and R. F. Schneider (*J. Amer. Chem. Soc.*, 1920, **42**, 32—36. Compare preceding abstract).—The reversible molecular heat of dilution has been determined for solutions of barium chloride of 3·2, 2·8, and 1·6 weight N, and for solutions of the mixed salts in equivalent proportions of 3·2, 1·6, 0·8, and 0·4 weight N. It is shown that the heat of dilution of the mixture of salts bears no simple additive relationship to the heat of dilution of the components at equivalent dilutions. The behaviour of barium chloride in this respect is therefore analogous to that of strontium chloride (*loc. cit.*). The experimental results can be explained on the same basis as the results obtained with the mixed strontium salts, namely, on the assumption of the formation of compounds of a higher order. J. F. S.

Relations between Relative Densities, Absolute Density, and Apparent Weight of Solutions. O. Chéneau (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 175—181).—For the interconversion of specific gravity results at 15°, from one basis of reference to another, a table has been compiled showing absolute densities (that is, 15° in vacuum/water at 4° in vacuum), and, in parallel columns, the corrections to be added or subtracted to arrive at corresponding values referred to any of the following bases: 15° in air/water at 15° in air, 15° in vacuum/water at 15° in vacuum, 15° in vacuum/water at 15·5° in vacuum, and 15° in air/water at 4° in vacuum. The values are given to five places of decimals, and range from 0·7 to 1·8. J. H. L.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. RUDOLF MEWES (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1919, **11**, 73—75, 91—93; from *Chem. Zentr.*, 1920, i, 104, 278. Compare Mewes and Neumann, A., 1919, ii, 493).—(*a*) The errors observed in the previous experiments are to be ascribed, in part, to the presence of impurities and consequent liquefaction.

In the second paper the author shows that Landolt's expression, $(n_{tp}-1):(n_{0\cdot760}-1)=d_{tp}$, is valid for low temperatures if errors due to partial condensation of the gas by surface action and partial liquefaction are eliminated. H. W.

Electrical Nature of the Cohesive Forces of Solid Substances. M. BORN (*Ann. Physik*, 1920, [iv], **61**, 87—106).—A mathematical paper in which relationships are deduced for the molecular forces existing in crystals of the alkali haloids. It was shown by Born and Landé (A., 1919, ii, 188) that the compressibility of these salts can be explained by the assumption that the ions exercise attractive and repulsive forces on one another in the sense of Coulomb's law, and that two ions exercise a repulsive force the potential of which is inversely proportional to the ninth power of the distance between the ions. The present calculations are based on this assumption. J. F. S.

Surface Tension of Mixtures of Water and Alcohol. JAMES BRIERLEY FIRTH (T., 1920, **117**, 268—271).

The Adhesion of Starch at Fluid Surfaces. I. Experiments with Starch Grains. F. B. HOFMANN (*Pflüger's Archiv*, 1917, **167**, 267—279; from *Physiol. Abstr.*, 1917, **2**, 541).—Potato-starch has been used to study the adhesion of solids when distributed between two immiscible liquids, and the conditions which influence this adhesion. J. C. D.

The Viscosity of Cæsium Salts in Glycerol-Water Mixtures. P. B. DAVIS (*Carnegie Inst. Pub.*, 1918, **260**, 97—98).—An extension of previous studies by Jones and others on the viscosity of solutions in glycerol and in binary mixtures containing glycerol, with special reference to those salts known to decrease the viscosity of water and of glycerol. Rubidium and cæsium iodides produced phenomenal lowering of the viscosity of glycerol. In these experiments the viscosities of cæsium nitrate and cæsium chloride were measured at 25° and 35°. Cæsium salts decrease the viscosity of glycerol-water mixtures more than rubidium salts. When salts of both rubidium and cæsium increase the solvent viscosity, as, for example, water and acetone or water and the alcohols, the cæsium salt produces a smaller increment than the rubidium salt. CHEMICAL ABSTRACTS.

The Sorption of Hydrogen by Palladium at Low Temperatures. JAMES BRIERLEY FIRTH (T., 1920, **117**, 171—183).

The Effect of Heating on the Absorptive Power of Sugar-charcoal for Sulphur Dioxide. RAMSAY MIDDLETON WINTER and HERBERT BRERETON BAKER (T., 1920, **117**, 319—321).

Influence of Temperature on the Adsorbability, the Colloid-precipitating Power of some Narcotics. R. BIERICH (*Pflüger's Archiv*, 1919, **174**, 202—217; from *Physiol. Abstr.*, 1919, **4**, 184).—The observation of Meyer and Overton of the partition-coefficients between oil and water was confirmed for the partition between cod-liver oil and water in the case of salicylamide and benzamide. The adsorption of narcotics by animal charcoal was found to be almost unaffected by alteration of temperature. In the investigation of the colloid-precipitating power it was found that with *iso*butyl alcohol, ethylurethane, propylurethane, benzamide, and salicylamide the precipitation of serum albumin by cobalt chloride is strengthened more at high than at low temperatures; the same applied for some of the narcotics with the sodium chloride precipitation of colloidal ferric hydroxide. The narcotic power as tested on tadpoles was always increased by rise of temperature. As regards benzamide and salicylamide this is opposed to the observation of Meyer that the threshold strength of the narcotic varies in the opposite direction to the oil–water partition-coefficient. J. C. D.

Adsorption by Precipitates. II. HARRY B. WEISER and EDMUND B. MIDDLETON (*J. Physical Chem.*, 1920, **24**, 30—73. Compare A., 1919, ii, 269).—The amount of adsorption of phosphate, citrate, tartrate, oxalate, sulphate, iodate, and dichromate ions by definite quantities of precipitated ferric oxide from a ferric oxide sol has been determined. It is shown that since the first process in the precipitation of a colloid by an electrolyte is the neutralisation of the charge by the adsorption of an ion of opposite charge, it follows that two adsorbing media are concerned in the process: the electrically charged particles and the electrically neutral particles. Accordingly, the total amount of a given ion carried down by a precipitated colloid is determined by (*a*) the adsorption by the electrically charged particles during the process of neutralisation, and (*b*) the adsorption of the electrically neutral particles during the process of agglomeration and settling. The failure to take the second cause into consideration has led to the erroneous conclusion that the amounts of all precipitating ions carried down by a precipitated colloid are equivalent. The adsorption of equivalent amounts of precipitating ions will neutralise a given amount of colloid, provided the stabilising effect of the ion having the same charge as the colloid is kept constant; but the amounts adsorbed by the neutralised particles will vary with the nature of the adsorbing medium, the nature of the adsorbed ion, and the concentration of the ion in the solution. The determination of adsorption values at the precipitation concentration, as a rule, will not give comparable results because of the variability in

the latter, and the consequent variability in the degree of saturation of the adsorbent in the adsorbed phase. The variations from strict equivalence in the adsorption values of Freundlich are probably due quite as much to the varying concentration and adsorbability of the ions as to the analytical errors. The ions mentioned above are strongly adsorbed by hydrated ferric oxide. The adsorption of univalent ions was relatively weak, so that the precipitate was readily peptised by washing. The amounts of the ions adsorbed are not even approximately equivalent. The phosphate ion is most strongly adsorbed, and the others follow the order: phosphate>citrate>tartrate > oxalate > sulphate > iodate > dichromate. The order of adsorption determined by analysis is entirely different from the order deduced from precipitation values on the assumption that the most strongly adsorbed ion precipitates in the lowest concentration. The latter order is: dichromate>tartrate>sulphate>citrate>oxalate>iodate>phosphate. In addition to the effect of the valency and the adsorbability of precipitating ions, the precipitating values are influenced by differences in the degree of ionisation of electrolytes, the hydrolysis of certain salts, the stabilising effect of the ion having the same charge as the colloid, the mobility of the ions which in certain cases decreases with dilution owing to increased hydration, the rate of coagulation, and the method of determining the critical concentrations. The order of precipitation values is the same for the acids as for their potassium salts except that the former precipitate in somewhat higher concentration than the latter owing to the stabilising effect of the strongly adsorbed hydrogen ion. There is apparently no connexion between the precipitation values and the ionisation constants of the acids investigated, probably because precipitation takes place at such small concentrations (0·0002—0·0008N). The order of precipitation values of the potassium salts is: ferrocyanide<ferricyanide<dichromate<tartrate < sulphate < oxalate <chromate<iodate<bromate < thiocyanate < chloride < chlorate <nitrate<bromide<iodide<formate. There is a tendency for ions of the highest valency to be most strongly adsorbed. That there are exceptions to this rule and that ions of the same valency are frequently adsorbed in widely varying amounts may be expected, since adsorbability is a specific property of the ions. J. F. S.

Attempt to Extend Planck's Theory of Dilute Solutions. P. Boedke (*Ann. Physik.* 1920, [iv], **61**, 334—352).—A theoretical paper in which Planck's thermodynamical function is considered in connexion with binary liquid mixtures with the object of obtaining expressions which shall represent the equilibrium conditions of such liquid pairs and give the saturation conditions. [See also Jahn, A., 1902, ii, 597.] J. F. S.

Polymerism of Dissolved Binary Salts. P. Walden (*Zeitsch. Elektrochem.*, 1920, **26**, 60—65).—The molecular weight of a number of binary salts has been determined by the cryoscopic

method at a series of concentrations in non-ionising solvents. As solvents, acetic acid, naphthalene, and diphenylamine were used, and as dissolved substances, tetra-amylammonium iodide, triphenylamylphosphonium iodide, tetrapropylammonium iodide, ammonium thiocyanate, tetramethylammonium thiocyanate, tetraethylammonium bromide, ethylammonium chloride, and tetraethylammonium iodide. From the results it is shown that depolymerisation occurs according to the expression $x=c^{\frac{1}{3}}.\text{const.}$, that is, the degree of association is directly proportional to the linear concentration or to the distance between the molecules. The molecular weight, M, of the dissolved salt conditions the dimensions of the constant, since $x=0{\cdot}305M^{\frac{1}{2}}/V^{\frac{1}{3}}$ or $x=0{\cdot}305M^{\frac{1}{2}}.C^{\frac{1}{3}}$. The influence of the nature of the solvent is shown by the fact that the degree of association x is inversely proportional to the dielectric constant E of the solvent, as shown by the expression $x=1{\cdot}92\sqrt{M}/EV^{\frac{1}{3}}$ or $x=1{\cdot}92.M^{\frac{1}{2}}C^{\frac{1}{3}}/E$. In view of the influence of the dielectric constant in the depolymerisation, the author puts forward the question: Are the products of depolymerisation oppositely electrically charged according to the scheme:

$$(MX)_2 \rightleftharpoons (MX)^{\cdot} + (MX)' \rightleftharpoons (M_2X)^{\cdot} + X' \rightleftharpoons 2M^{\cdot} + 2X'?$$

J. F. S.

Influence of the Molecular Size of Electrolytes on the Conductivity and the Ionic Velocity of the Ions: Solvation of Ions in Non-aqueous Solutions. P. Walden (*Zeitsch. Elektrochem.*, 1920, **26**, 65—71).—It is shown that a large number of binary salts, mainly iodides, in a number of non-aqueous solvents follow the relationship $\lambda_\infty \eta_\infty \sqrt{M}=\text{const.}=11{\cdot}15$, where λ_∞ is the limiting conductivity of a salt with molecular weight M in the solvent under investigation, and η_∞ is the viscosity of the solvent. If these salts are regarded as normal, that is, neither associated nor solvated, it becomes possible to determine the degree of solvation of other salts with a fair degree of accuracy. As a control of the values obtained from the formula deduced by Herzog from Einstein's relationship (A., 1911, ii, 23), $\lambda_\infty \eta_\infty V^{\frac{1}{3}}=\text{const.}$ may be used. Both equations give solvation values which are practically identical for the ions examined. J. F. S.

Is the Migration Velocity of the Ions of an Electrolyte Extremely Large when the Solvent is Capable of Forming Similar Ions? P. Walden (*Zeitsch. Elektrochem.*, 1920, **26**, 72—76).—A theoretical paper in which the conductivity and mobility of the ions of salts, which furnish one ion similar to one of the ions of the solvent, have been considered. The solvents considered are pyridine, formic acid, acetic acid, aniline, *m*-chloroaniline, nitromethane, methyl thiocyanate, hydrocyanic acid, ammonia, formamide, and nitric acid. The results show that the titular question is to be answered in the negative, and that if there is any influence of the solvent on the dissolved substance in this respect, it only occurs in a few exceptional cases. J. F. S.

Dissociating Powers of Free and Combined Water. G. FRED ORDEMAN (*Carnegie Inst. Pub.*, 1918, **260**, 119—127).—The conductivities of two isohydric solutions were measured, and the measurements repeated after the addition of a third salt (in three different concentrations). The following series of salts were used: (*a*) isohydric solutions of *M*-potassium chloride and 0·695*M*-calcium chloride, before and after the addition of sodium, potassium, ammonium, magnesium, calcium, or strontium chloride; (*b*) isohydric solutions of *M*-sodium chloride and 0·597*M*-calcium chloride, the addendum being sodium, ammonium, magnesium, calcium or strontium chloride, or potassium nitrate; (*c*) isohydric solutions of *M*-sodium nitrate and 0·681*M*-calcium nitrate, the addendum being sodium, potassium, ammonium, magnesium or calcium nitrate, or potassium chloride; (*d*) isohydric solutions of 0·5*M*-sodium nitrate and 0·310*M*-calcium nitrate, the addendum being as in (*c*); (*e*) isohydric solutions of *M*-potassium nitrate and 0·698*M*-calcium nitrate, the addendum being sodium, potassium or strontium nitrate, or potassium or sodium chloride. For every pair of solutions, the suppression of the conductivity is more pronounced in the hydrated solutions, showing that the added salt dissociates more in the non-hydrated solutions than in the comparable, isohydric solutions of the hydrated salts. The repression of the ionisation of the hydrated salts added is much greater than that of comparable quantities of non-hydrated salts in both isohydric solutions of every pair studied. A few added salts, having no common ion, show irregular results. The combined water (of hydration) in the solution of a hydrated salt is assumed to possess less ionising power than the uncombined water, hence the salt added would be less dissociated. The hydrated salts used as addenda are less dissociated than the other addenda, because the water of hydration now exists in both of any pair of solutions. The dissociation, however, is always less in the solution of the hydrated salt of any pair, because of the smaller dissociating power of the water of hydration already present in that solution.

CHEMICAL ABSTRACTS.

The Ultimate Structure of Isomorphous Substances. F. RINNE (*Centr. Min.*, 1919, 161—172).—From the results of the *X*-ray analysis of the crystal structure of a number of substances, the author has calculated the absolute atomic or molecular volumes of the substances comprising a number of isomorphous series. The substances dealt with are the cubic elements aluminium, copper, silver, gold, and lead, the rhombohedral carbonates of magnesium, calcium, manganese, iron, zinc, and cadmium, and the haloids of lithium, sodium, potassium, rubidium, and cæsium. From a comparison of the Röntgen-ray diagrams of a large number of minerals, which are usually isomorphous mixtures, with those of pure substances, it is concluded that there is no essential difference between their structures; that is, the *X*-ray evidence favours the view that in isomorphous mixtures the dispersity is so great that

it is highly probable that the vicarious constituents replace one another atom for atom or group for group in the lattice structure of the crystal. The importance for isomorphism of the chemical nature, and especially of the valency, of the vicarious atoms or atomic groups is insisted on. This factor is often of more importance in determining isomorphism or miscibility than molecular volume. Thus, in the case of the above elements, although the edge of the fundamental lattice is practically of equal length for aluminium, silver, and gold, and considerably less for copper, silver and gold are perfectly miscible together, but only slightly so with aluminium. In the case of the haloids of the alkali metals, the miscibility varies with the temperature to a much greater extent than would be expected were the dimensions of the fundamental lattices the ruling factor. The author regards the mixed crystal state as one intermediate between a physical mixture and a true chemical compound. E. H. R.

Von Weimarn's Theory of the Colloidal State. E. H. BUCHNER and J. KALFF (*Rec. trav. chim.*, 1920, **39**, 135—144).—The authors consider that von Weimarn's theory of corresponding states in the formation of precipitates is untenable. They show that his law giving the relationship between "the coefficient of precipitation," on which the form of the precipitate depends, the solubility of the substance precipitated, and the amount of the precipitate formed is incorrect in the cases of such precipitates as calcium fluoride, barium fluoride, and calcium sulphate in comparison with barium sulphate, and in the cases of silver chloride, bromide and iodide, and lead iodide. Further, that in the case of such precipitates as aluminium hydroxide, the conditions cannot be expressed by any formula. Whilst his theory may have some value qualitatively, his law of corresponding states is not confirmed by quantitative experiments. W. G.

Swelling and Solution of Aleuron. MARIAN O. HOOKER and MARTIN H. FISCHER (*Kolloid Zeitsch.*, 1920, **26**, 49—58).—The amount of swelling of aleuron (a mixture of plant proteins) occasioned by water, dilute solutions of hydrochloric, nitric, sulphuric, lactic, formic, and tartaric acids, hydrochloric acid mixed with various quantities of the chlorides of sodium, potassium, iron, aluminium, ammonium, copper, magnesium, calcium, and strontium respectively; hydrochloric acid mixed with potassium bromide, nitrate, iodide, acetate, thiocyanate, tartrate, and citrate respectively; and hydrochloric acid mixed with carbamide, methyl alcohol, ethyl alcohol, dextrose, and sucrose respectively, has been measured. The amount of aleuron dissolved by the above-named solutions has also been determined. A similar series of experiments has been carried out with sodium hydroxide solutions and with sodium hydroxide solution to which the above-named substances have been added. It is shown that aleuron behaves, as

regards its swelling and solution, in much the same way as gelatin, fibrin, blood serum, and gluten. It swells more in acid and alkali solutions than in water, but the amount of swelling does not run parallel with hydrogen- or hydroxyl-ion concentration. The swelling is reduced, not only by neutralisation of the acid or alkali, but also by the addition of neutral salts. The greater the concentration of the added salt, the greater the reduction of the swelling. Non-electrolytes do not influence the swelling in either acid or alkali solution. The solubility of aleuron in acids and in alkalis is also greater than in water, but it does not run parallel with the swelling. Some salts increase the solubility, whilst others reduce it in both acid and alkaline solutions, but there is no parallelism between solubility and swelling. The results indicate that hydration and solution of an albuminous substance or mixture of albuminous substances, although often connected and often occurring in the same sense, yet are not identical processes. Each follows its own particular laws. J. F. S.

Influence of the Concentration of Electrolytes on some Physical Properties of Colloids and Crystalloids. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 273—296).—When alkali or neutral salt is added to a 1% solution of sodium gelatinate separated from distilled water by a collodion membrane, the rate of diffusion is diminished. This depressant action is greater when the cation of the added electrolyte is bivalent than when it is univalent. When a neutral $M/256$-solution of a salt with univalent cation is separated from distilled water by a collodion membrane, and an alkali or neutral salt is added, the diffusion of water is also depressed in proportion to the amount added. It can be shown that under these conditions water diffuses through the membrane in the form of positively charged particles. In the case of the diffusion of water into a neutral salt with univalent or bivalent cation, the effect of the addition of electrolyte on the rate of diffusion can be explained on the basis of the influence of the ions on the electrification and the rate of diffusion of the electrified particles of water. Since the influence of the addition of electrolyte seems to be the same in the case of solutions of metal gelatinate, the question arises whether this influence cannot also be explained in the same way, and, if this be true, the further question can be raised whether this depressing effect necessarily depends on the colloidal character of the gelatin solution, or whether in both cases the same property of matter is not being dealt with, namely, the influence of ions on the electrification and rate of diffusion of water through a membrane.

The curve representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water from solvent into the solution through the membrane is similar to the curve representing the permanent osmotic pressure of the gelatin solution. The diffusion of water as negatively charged particles into a solution of gelatin chloride is depressed by addition of an acid or

neutral salt. This is also found to be true when the diffusion takes place into a solution of $M/512$-Al_2Cl_6. J. C. D.

Influence of a Slight Modification of the Collodion Membrane on the Sign of the Electrification of Water. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 255—271).—Collodion membranes which have received one treatment with 1% gelatin solution show for a long time afterwards a different osmotic behaviour from untreated membranes. This difference shows itself only towards solutions of those electrolytes which have a tendency to induce a negative electrification of the water particles diffusing through the membrane. When solutions of salts with tervalent cation are separated from water by collodion membranes treated with gelatin, water diffuses rapidly into the solution, whilst no water diffuses when the collodion membrane has received no gelatin treatment. Solutions of acid separated from water by treated membranes show negative osmosis, whereas with untreated membranes positive osmosis occurs. These differences only occur in that range of concentrations of electrolytes inside of which the forces determining the rate of diffusion of water through the membrane are predominantly electrical, that is, from 0 to about $M/16$. The differences in the osmotic behaviour of the two types of membrane are not due to differences in permeability, but are rather due to the fact that water diffuses into solutions of tervalent cations or acids through gelatin-treated membranes as negatively charged particles, whilst in the case of non-treated membranes the charge is positive. Treatment of the membranes with caseinogen, egg-albumin, blood-albumin, or edestin has the same effect, but treatment with peptone from egg-albumin, alanine, or starch has no such effect. J. C. D.

Colloidal Electrolytes. Soap Solutions and their Constitution. JAMES W. MCBAIN and C. S. SALMON (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 44—65; *J. Amer. Chem. Soc.*, 1920, **42**, 426—460).—Colloidal electrolytes are solutions of salts in which an ion has been replaced by a heavily hydrated multivalent micelle carrying an equivalent sum total of electric charges, and also serving as an excellent conductor of electricity. This new class of electrolytes probably includes most organic compounds containing more than eight carbon atoms, and capable of forming ions, also acid and alkali solutions of proteins, dyes, indicators, sulphonates, soaps, alkali tungstates, zincates, tellurates, and silicates. The constitution of solutions of the sodium and potassium salts of behenic, stearic, palmitic, myristic, lauric, decoic, octoic, hexoic and acetic acids has been investigated. The vapour pressure and elevation of the boiling point have been ascertained by the dew-point method for solutions of the above-named salts at concentrations $0{\cdot}2N$—$3{\cdot}0N$. From the results, coupled with osmotic and conductivity data previously published (T., 1914, **105**, 435), the concentration of crystalloid constituents and the concentration of colloid constituents are deduced. It is shown that, in N-solutions,

in every case colloid material is present; in the case of the hexoate, 15% is present as colloid, whilst with potassium stearate, 99% is colloid. The amount of colloid decreases rapidly with decrease in concentration, and it apparently becomes inappreciable with $N/5$-laurate solutions. The ionic micelle are regarded as either (in the case of palmitate) an agglomeration of palmitate ions heavily weighted by water as a complex solvate, $(P')_n.(H_2O)_m$, or, and more probably, a collection of all, or nearly all, the colloid in the ionic micelle, $(NaP)_x.(P')_n(H_2O)_m$. J. F. S.

Penetration of Electrolytes into Gels. I. Penetration of Sodium Chloride into Gels of Agar-agar containing Silver Nitrate. WALTER STILES (*Biochem. J.*, 1920, **14**, 58—72).—The penetration of sodium chloride from solutions of various concentrations ($5N$—$0{\cdot}05N$) into agar gels has been followed by the indicator method. When silver nitrate is present in the gel, the entrance of sodium chloride into the gel is marked by the formation of silver chloride, and the progress of the chloride into the gel is indicated by the forward movement of the sharp line of demarcation between the silver chloride in the gel and the unprecipitated silver salt. The distance this line of demarcation has moved forward in any time is termed the penetration. It marks the position of a definite concentration of chloride, namely, the saturation concentration of silver chloride. The penetration of sodium chloride into agar gels containing silver nitrate is, within wider limits, proportional to the square root of the time. If P is the penetration in a time t, $P/\sqrt{t}$ = constant for any particular gel and any particular concentration of penetrating salt, and is termed the penetration factor. The rate of penetration is dependent on the initial concentration of the penetrating salt, the higher the concentration of the salt the more rapid the penetration. The concentration of the gel itself appears to exercise little influence on the rate of penetration, but, owing to the probability of actions between the silver salt and the gel, and hence doubt as to the true active concentration of the silver salt in the gel, the influence of concentration of the gel must be left an open question. In any case, the influence cannot be great in gels containing between 1 and 4% agar. The expression obtained by von Fürth and Bubanovič (A., 1919, ii, 13) to indicate the relationship between the penetration, time, and concentration of the penetrating salt only holds in very special cases and between narrow limits, and is even then only very approximate. The following more general empirical relationship is deduced, $P/\sqrt{t} = k \log c + k'$, where c is the initial concentration of the penetrating salt, k a constant depending on the nature of the penetrating salt and also, although to a slight extent, on the nature of the gel content, and k' a second constant depending mainly on the concentration of silver nitrate in the gel. J. F. S.

Adsorptive Stratification in Gels. III. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 29—41. Compare A., 1919, ii, 139).—A discussion of the supersaturation and the adsorption

theory of the Liesegang phenomenon in gels. The author supports the adsorption theory by a number of experimental facts. The formation of bands usually ceases long before the bottom of a tube is reached. The hypotonic reagent is invariably so strong that this effect can only be due to the solute in the gel having been exhausted from the lower regions of the tube. This fact also controverts the deduction from the supersaturation theory, that the diffusion of the solute in the gel is negligible.

With certain colloidal precipitates, such as manganese sulphide, in agar, a tendency is observed to form large spherical aggregates which have much the same structure and density as the bands, except that they frequently show concentric banding. When one of these spherical aggregates begins to form in the zone where a band will shortly appear, the band does not extend to join the sphere, but a spherical cavity, 2—3 mm. wide, is left surrounding the concretion, from which the surface of the cavity is everywhere equidistant. This effect must be due to the solute having been exhausted from the neighbourhood of the aggregate. Its spherical form implies that nutrient material has accrued equally from all directions. J. F. S.

Mutual Action of Sols. WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 21—29).—A theoretical paper in which it is shown that when positively charged gelatin is mixed with a negatively charged sol, or negatively charged gelatin with a positively charged sol, there may be precipitation over a range of relative concentrations. When two sols, peptised by water, are mixed, the mutual adsorption may decrease the adsorption of water to such an extent that precipitation takes place. There may be, and often is, mutual adsorption when two sols having the same electrical charge are mixed. The mutual adsorption of positively charged ferric oxide and positively charged gelatin in ammonia solution gives a different product from the mutual adsorption of positively charged ferric oxide and positively charged gelatin to which ammonia is subsequently added, inasmuch as in the first case precipitation is brought about, whilst in the second there is no precipitation. J. F. S.

[Physical Chemical Analysis of Metal Hydrosols.] An Explanation. RICHARD ZSIGMONDY (*Kolloid Zeitsch.*, 1920, 26, 67—69).—Polemical; an answer to Pauli's criticism (this vol., ii, 168) of certain parts of a paper by Varga. J. F. S.

Rôle of Valency in the Coagulation of Suspensoids by Electrolytes. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1920, 26, 69—81. Compare this vol., ii, 168).—The various theories which have been put forward to explain the function of valency in the coagulation of suspensoids are summarised, and the precipitation values of a large number of electrolytes are collected from various sources and tabulated. From the absorption theory of Freundlich,

an expression is deduced which gives a quantitative relationship between valency and precipitating power. This has the form $1/c_1:1/c_2:1/c_3 \ldots = 1:2^n:3^n \ldots$, in which c_1, c_2, and c_3 are the precipitating values of uni-, bi-, and ter-valent electrolytes, and n is a constant. It is shown that none of the theories hitherto put forward satisfactorily accounts for the coagulation of electrolytes. It is shown that the rôle of valency as the determining factor in coagulation processes has been considerably overestimated. This follows from the facts that (1) the precipitating values of electrolytes of the same valency differ considerably, (2) univalent electrolytes in some cases have smaller precipitating values than bivalent electrolytes, and (3) salts of different valencies fall into the same group with respect to their precipitating values. J. F. S.

Precipitation of Congo-rubin by Electrolytes. WOLFGANG OSTWALD (*Koll. chem. Beihefte*, 1920, **26**, 92—102. Compare A., 1919, ii, 187, 400).—A continuation of previous work (*loc. cit.*). It is shown that the behaviour of Congo-rubin toward electrolytes in respect of Schulze's rule is exactly the same as that of inorganic hydrosols. The behaviour of Congo-rubin in respect of its colour changes in the presence of electrolytes is of the same nature and depends on the same causes as the colour changes of inorganic hydrosols, for example, the colour changes of gold sols, or, in other words, the phenomenon is of colloidal chemical character.

J. F. S.

Equilibria in Solutions containing Mixtures of Salts. The System Water and the Chlorides and Sulphates of Sodium and Magnesium at 25°. W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1920, **12**, [ii], 164—167).—Previous work on this subject indicates that the solid phases to be expected at 25° are $MgSO_4,7H_2O$, $MgSO_4,6H_2O$, $MgSO_4,H_2O$, $Na_2SO_4,10H_2O$, Na_2SO_4, $MgCl_2,6H_2O$, NaCl, and $MgSO_4,Na_2SO_4,4H_2O$ (blödite). In ascertaining the limits of the fields representing the composition of all the solutions which can be in equilibria with each of the eight solid phases, the composition of solutions saturated with respect to $MgSO_4,7H_2O$, $Na_2SO_4,10H_2O$, $MgCl_2,6H_2O$, and NaCl was determined, and the ends of two axes at right angles, one to represent the relative proportions of $MgSO_4$ and NaCl, and the other of Na_2SO_4 and $MgCl_2$, were fixed. The solubility of each of the former four salts in solutions containing increasing concentrations of a second salt which yields a common ion was determined up to the point at which a second solid phase appeared, and thereby a number of points intermediate between the extremities of the two axes, representing solutions in equilibrium with two solid phases, were fixed. Further, starting with solutions saturated with respect to two solids, the composition of solutions saturated with respect to each pair of solids, in the presence of increasing concentrations of that salt which yielded a fourth ion, was determined up

to the point at which a third solid separated. The results are shown in a curve, in which the horizontal axis is used to represent the number of mols. of $MgSO_4$ and NaCl, and the vertical axis the number of mols. of $MgCl_2$ and Na_2SO_4, per 1000 mols. of water, and tables are given showing the composition of all these solutions which represent critical points. S. S. A.

Reaction Isochore and Velocity of Reaction from the Statistical Point of View. M. POLÁNYI (*Zeitsch. Elektrochem.*, 1920, **26**, 49—54).—A theoretical paper in which it is shown that the velocity constant of a reaction of the type $A + B_2 \rightleftharpoons AB + B$ in the endothermic direction is given by the product of the number of collisions and the equilibrium constant, and in the reverse direction it is the same as the number of collisions. These results are deduced from the assumption that it is just as likely after a collision between A and B_2, that the particles react, or that they are dispersed without a reaction taking place. The results of the theoretical investigation are tested by means of the experimental results of Bodenstein and Lind on the reaction $Br + H_2 \longrightarrow BrH + H$ (A., 1907, ii, 76), and found to be in accordance with the experimental facts. J. F. S.

Influence of Pressure on the Temperature of Explosion. G. TAMMANN (*Nach. Ges. Wiss. Göttingen*, 1919, 220—224; from *Chem. Zentr.*, 1920, i, 146).—The explosive material is contained in a small glass tube open at one end, and is placed in a steel cylinder filled with mercury; the latter is connected with a spring manometer and pressure pump. The cylinder is heated in an oil-bath provided with an efficient stirrer, the temperature of the bath being observed from minute to minute. Tables are given showing the rate of heating in degrees per ten minutes before attaining the temperature of explosion, the weight of explosive, the pressure and temperature at which explosion occurs, the differences in pressure before and after the explosion, and the sudden rise of pressure during the explosion. The temperature of explosion of moist glyceryl nitrate varied somewhat considerably at constant pressure increase of the latter by 2500 kilos. per sq. cm. appeared to depress the temperature of explosion by 8·4°, but the variation lies within the limits of experimental error. With dry glyceryl nitrate, the variations are less marked, but a distinct influence of the pressure on the temperature of explosion is not observed; a similar effect is still less certain in the case of a mixture of tetranitromethane (2 mols.) and benzene (1 mol.). With tetranitromethane (2 mols. and naphthalene (1 mol.), an increase in pressure of about 200 kilos per sq. cm. causes an elevation of 5·7° in the temperature of explosion. The influence of pressure on the temperature of explosion of liquid explosives is determined by the effect of pressure on the conductivity for heat of the material itself and its environment, and by alteration in the chemical-kinetic conditions, such as the increase in the number of molecular collisions caused b

isothermal increase in pressure as a consequence of the increase in volume of the explosive. H. W.

Difference in Chemical Activity of Free and Semi-combined Water as Illustrated by the Effect of Neutral Salts on the Hydrolysis of Acetic Anhydride. GERALD C. CONNOLLY (*Carnegie Inst. Pub.*, 1918, **260**, 131—143).—In extension of the work of Holmes and Jones (*ibid.*, 1915, **230**) on the effect of salts on the hydrolysis of methyl acetate and methyl formate, the action of strongly hydrated and of slightly hydrated salts on the hydrolysis of acetic anhydride has been studied with the object of determining whether any chemical difference exists between free and combined water. Care being taken always to keep the water content constant, M-, $0{\cdot}5M$-, and $0{\cdot}25M$-solutions of various salts (potassium, sodium, calcium, magnesium, barium, and strontium chlorides, sodium and magnesium sulphates, potassium and sodium nitrates) at 15° and at 25° were treated with acetic anhydride, aliquot portions were removed at various intervals, and the acetic acid estimated. The amount of acetic acid present in mixtures of the acid and its anhydride was estimated by adding aniline and titrating the total acetic acid with sodium hydroxide. The concentration of the anhydride was 5%, and in no case did the time exceed sixty minutes at 15° and forty minutes at 25°, since the hydrolysis by water was practically complete.

All the salts examined, excepting sodium and magnesium sulphates, have in the case of the greater concentrations a retarding influence on the hydrolysis, the retardation diminishing with increasing salt dilution. The four non-hydrated salts have practically the same retarding effect on the hydrolysis. The hydrated salts, excepting magnesium chloride, produce greater hydrolysis than the non-hydrated salts, and with the more dilute solutions there is an appreciable acceleration of the hydrolysis of the anhydride over that due to water alone. Sodium and magnesium sulphates at all concentrations have a marked accelerating effect on the hydrolysis. Calcium, strontium, and barium chlorides also exert an accelerating influence in the more dilute solutions. The results with magnesium chloride and sulphate were inconclusive, the former resembling the non-hydrated salts in retarding the hydrolysis at all dilutions. CHEMICAL ABSTRACTS.

The Alkaline Hydrolysis of Tartaric Ester. ANTON SKRABAL and ERNA SINGER (*Monatsh.*, 1919, **40**, 363—375).—The rate of hydrolysis of methyl tartrate by a mixture of sodium carbonate and sodium hydrogen carbonate has been measured, after the procedure necessary for the attainment of satisfactory results had been worked out in the case of methyl acetate. Referred to $[OH]'=1$ and at 25°, the constants for the first and second stages in the hydrolysis of methyl tartrate are $k_1=206$ and $k_2=14{\cdot}7$ respectively, whilst for methyl acetate $k=5{\cdot}4$. J. K.

Catalysis of Hydrogen and Oxygen Mixtures at the Ordinary Temperature by Moistened Contact Substances. II. The Platinum Metals as Hydrogen Carriers. K. A. HOFMANN and LOTTE ZIPFEL (*Ber.*, 1920, **53**, [*B*], 298—314. Compare Hofmann and Ebert, A., 1917, ii, 25).—The results may be summarised in the following manner.

Mixtures of oxygen and hydrogen are catalysed at palladium, platinum, or iridium surfaces at very different rates, depending on the exact extent, at the moment, to which they are charged with gas. Pre-treatment with oxygen is thirty to fifty times as effective in the case of palladium, three times with platinum, and three to ten times with iridium as is pre-treatment with hydrogen. The greater activity caused by charging with oxygen is not brought about by the adsorbed or occluded gas serving as a source for the formation of water, since the amount of metal required for catalysis is insufficient to produce this effect, but depends on the production of a "fresh" hydrogen-metal combination, which, in the cases of palladium and platinum, is far more active than an "aged" preparation. The catalyst shows greater activity in proportion as this "fresh" condition is more rapidly and completely developed. In the case of iridium, another factor is involved, since the metal, in presence of gases containing excess of oxygen, can function as an active oxygen electrode.

The close parallelism between catalytic and electromotive activity indicates that both effects are to be ascribed to the same cause. This probably depends on the presence of free or metallically-dissolved hydrogen atoms, which cause the hydrogen potential and ultimately combine with the oxygen of the gas mixture to form water. Under the experimental conditions adopted, an active oxygen electrode is only formed with finely divided iridium when the oxygen concentration is high; platinum and palladium behave entirely as hydrogen electrodes.

The maximal velocity of formation of water is not invariably observed when the gases are used in the proportion of hydrogen (2 vols.) to oxygen (1 vol.), but, according to conditions, may occur at a greater or smaller oxygen concentration, according as the catalyst becomes more or less rapidly saturated with hydrogen. If the catalyst can also function as an oxygen electrode, as in the case of finely-divided iridium, a second maximum may occur with a higher oxygen content in the gas.

It may be generally stated that the surface does not show its greatest catalytic activity when hydrogen and oxygen are absorbed according to the measure of their combination at an electrically neutral electrode, but that the maximum possible hydrogen or oxygen potential must be "freshly" developed in order to react with the gaseous mixture at the maximum rate. H. W.

A Relation among the Atomic Weights of Chemical Elements. SUMINOSUKE ONO (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 231—236).—The atomic weight (A) may be given by a

formula, $A = N'^{\eta}$, where $\eta = 1.204$ and N' is roughly equal to Moseley's atomic number $+2$ or Rydberg's ordinals. For the more exact calculation of the atomic weight, N'^{η} may become a more complicated function, and N' may be identical with neither the atomic numbers nor the ordinals. CHEMICAL ABSTRACTS.

The Derivation of Molecular and Atomic Weights from Vapour Densities in Chemical Teaching. W. MANCHOT (*Chem. Zeit.*, 1920, **44**, 153—154).—An academic discussion on the most suitable formulæ for expressing the relation between molecular weights and gas densities with respect to water, air, and hydrogen in teaching chemistry. E. H. R.

The Law of the Harmonic Triangle in Chemical Reactions. EDUARD SCHMIZ (*Ber. Deut. pharm. Ges.*, 1920, **30**, 27—33). —The numerical relationships shown in a previous paper to hold between the atomic weights of a number of the elements (A., 1919, ii, 460) are now shown to hold also between the atomic and molecular weights of substances taking part in simple inorganic reactions. These relationships are those holding between the sides and hypotenuse of an isosceles right-angled triangle, the radius of the inscribed circle and that of the circle circumscribed about the squares erected on the sides of the triangle. It is claimed that, in simple cases, unless such a relationship holds between the molecular weights of substances, interaction between them cannot take place. E. H. R.

Structure of the Atomic Nucleus. E. GEHRCKE (*Ber. Deut. physikal. Ges.*, 1919, **21**, 779—784).—A theoretical paper in which the author formulates the constitution of the nucleus of the helium, lithium, glucinum, boron, nitrogen, and carbon atoms. The helium nucleus consists of two electrons and four hydrogen ions. In the case of lithium, the nucleus consists of four electrons situated at the corners of a regular tetrahedron, and seven hydrogen ions situated one at the centre of gravity of the tetrahedron, one at each corner of the tetrahedron, and two in an orbit close to the tetrahedron and at some distance from the outer electron ring. This nucleus is capable of accounting for the doublet series of the lithium spectrum. Glucinum possesses a nucleus consisting of five electrons situated one at the centre of gravity and one at each of the corners of a regular tetrahedron, and nine hydrogen ions situated one in the middle of each of the edges of the tetrahedron and the remaining three in an orbit surrounding the tetrahedron. This nucleus is capable of explaining triplet series of the glucinum spectrum. Boron has a nucleus composed of six electrons situated one in the middle of each of the edges of a regular tetrahedron, and eleven hydrogen ions situated one at the centre of gravity of the whole, one on the outside of each of the nuclear electrons, and one at each of the corners of the tetrahedron. The nucleus of carbon consists of six electrons situated as in the case of boron, one in

the middle of each of the edges of a regular tetrahedron, and twelve hydrogen ions, two of which are attached to each of the electrons. A nucleus so constructed accounts for the tetrahedral directions of the carbon valencies, since it will possess four electrostatic lines of force in these directions. Nitrogen is regarded as having a nucleus composed of seven electrons and fourteen hydrogen ions, which are grouped into three helium nuclei in an orbit surrounding one electron with two hydrogen ions attached to it. Constructing, further, after the manner of nitrogen, the nucleus oxygen is regarded as a ring of four helium nuclei, fluorine as four helium nuclei in a ring round an H_3^+ ion, and neon as a ring of four helium nuclei round a single helium nucleus. J. F. S.

Condition of Dissociation of the Gases of the Fixed Stars. JOHN EGGERT (*Physikal. Zeitsch.*, 1919, **20**, 570—574).—A theoretical paper in which, on the basis of the Nernst heat theorem, the relationship between the dimensions of the chemical constants deduced by Sackur, Tetrode, and Stern, and the Bohr atomic theory, the degree of dissociation of the atoms into nucleus and electrons, possible at temperatures between 10^6 and 10^{70} and pressures of 10^7 atm., is investigated. The calculations show that, considering only one type of atomic model, the maximum dissociation would consist in the separation of the two outermost rings of electrons, that is, of sixteen electrons. From this, it follows that the mean atomic weight of the gases of the fixed stars is 3·3, a value which is very near that (2·8) deduced by Eddington in his theory of the structure of the fixed stars. J. F. S.

Atomic Nuclei and α-Radiation. HANS TH. WOLFF (*Ann. Physik*, 1919, [iv], **60**, 685—700).—A theoretical paper in which a theory of the structure of the atomic nucleus and the forces operative in the nucleus is put forward. The nucleus has a disk-like form and is made up of concentric rings. With the exception of the outermost ring, they consist of singly charged hydrogen atoms and doubly charged helium atoms, which are rotating round the middle point. Outside these charged atoms, in the outermost ring, rotate the electrons. The positive charges are assumed to exert an attraction on one another when they are at certain distances apart, and thereby effect the stability of the nucleus. At small distances, however, a repulsive force becomes operative. On this assumption, it is shown that one of the two potential formulæ,

$$P=L(1/R-A_2/R^2+A_3/R^3)$$

and $P=L(1/R-A_3/R^3+A_5/R^5)$, represents the reciprocal action of the positive charges in the atomic nucleus. Expressions are deduced for calculating the potential and field of force which a rotating charge will generate in a point in the same plane, but in a ring outside itself. The conditions of stability after movement are worked out for a point which attracts a rotating charge according to either of the above formulæ. Both potential formulæ are applied to the atomic nucleus of the radium atom, and the constants

determined so that they are in keeping with the expulsion of an α-radiation of the experimentally determined velocity.

J. F. S.

Analysis of an Electron-transference Hypothesis of Chemical Valency and Combination. JOHN MARSHALL (*Proc. Roy. Soc. Edin.*, 1919, **39**, [3], 209—233).—A mathematical investigation of refractive indices based on the Thomson model atom, in which account is taken of the effect of the positive electrification as well as of the electrons, and of the fields of electrical action between the atoms of a molecule. The results are in moderate agreement with experiment. J. R. P.

The Octet Theory of Valence and its Applications with Special Reference to Organic Nitrogen Compounds. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1920, **42**, 274—292).—The octet theory of valence, which has been described in previous papers (Lewis, A., 1916, ii, 310; Langmuir, A., 1919, ii, 506), is here applied particularly to organic nitrogen compounds, although the general application of the theory to inorganic nitrogen compounds and to salts is discussed.

The number of available electrons in the outside shell of any atom is usually given by the ordinal number of the column of the periodic table in which the element is found. The number, which may be represented by E, corresponds with the maximum positive valence of the ordinary valence theory, and is one for sodium, four for carbon, five for nitrogen, six for oxygen, and seven for chlorine. It is readily proved that the octet theory is entirely in agreement with the ordinary valence theory whenever the ordinary formulæ are based on valences of unity for hydrogen and $8-E$ for each other element. Thus the ordinary formulæ agree with those of the octet theory whenever the following valences are adopted: hydrogen, one; carbon, four; nitrogen and phosphorus, three; oxygen and sulphur, two; chlorine, bromine, etc., one. On the other hand, all formulæ in which valencies different from these have been used require modification according to the octet theory. The application of the octet theory to the following compounds, among others, the formulæ of which require modification, is particularly discussed: sodium chloride, Na^+Cl^- (the co-valence of both atoms is zero); ammonium chloride, $(NH_4)^+Cl^-$ (the nitrogen is quadricovalent); triphenylmethyltetramethyl ammonium, $(NMe_4)^+[CPh_3]^-$ (the nitrogen is quadricovalent, whilst the central carbon atom in the anion is tercovalent); diazophenol, $R{<}\begin{smallmatrix}O\\|\\N{:}N\end{smallmatrix}$; diazonium compounds, $(R{-}N{\equiv}N)^+OH^-$ or $R{-}N{\equiv}N{\cdot}OH$; triazo-compounds, $R{-}N{=}N{\equiv}N$; hydroxylamine, $H_2N{\cdot}OH$ or $H_3N{-}O$.

According to this theory, all salts are completely ionised even before they are brought into solution. This conclusion is, moreover, in agreement with the recent work of Milner, Ghosh and

others; it explains why there are weak acids and weak bases, but no weak salts.

The known cases of isomerism, including stereoisomerism, of nitrogen, phosphorus, and sulphur compounds are in full accord with the octet theory.

The fact that organic cyanates, cyanides, and nitrites exist in two isomeric forms whilst the corresponding inorganic salts exist in only one form is explained, since the nulcovalent atoms of the metals in the inorganic compounds are not attached to definite atoms of the acid radicles.

The available data on phosphonium, arsonium, sulphonium, and oxonium compounds are in full accord with the octet theory, which gives for these compounds constitutions closely resembling those previously assigned by Werner. H. W.

Accelerated Filtration through Filter-paper. G. Bruhns (*Chem. Zeit.*, 1920, **44**, 207).—A filter-paper, folded in the usual way, is placed in a funnel, and the loose end of the three-fold layer is turned back and pressed against the side of the funnel; this folding back is repeated several times, so that the greater part of the interior of the funnel is covered by only one thickness of paper. In the ordinary way of using a filter, one-half of the funnel is covered by a threefold layer of paper. W. P. S.

Small Generator for Acetylene Bunsen Burners. P. Askenasy (*Zeitsch. Elektrochem.*, 1920, **26**, 32).—An acetylene generator is designed which with one charge of carbide will feed a large bunsen burner with acetylene for six hours. J. F. S.

[Lecture Experiment.] A Chemical Model of the Excitation Process. Max Verworn (*Pflüger's Archiv*, 1917, 167, 289—308).—A mixture of pure, vacuum-distilled nitric acid and 40% formaldehyde solution possesses considerable lability, and will react with explosive violence by the action of certain stimuli. The reaction is an oxidative decomposition of the formaldehyde to carbon dioxide and water. The mixture will remain unchanged at ordinary temperatures, but on addition of nitrous oxide, colloidal platinum, or on warming there is first a latent period during which no change occurs, which is followed by the violent reaction. Cooling the mixture, or the addition of water, or a carbamide solution will inhibit the process. If the mixture is placed in a long tube, and one part is locally stimulated, the reaction will proceed along the whole tube in the form of a wave. The mixture is an "isobolic" system, and obeys the "all or nothing" law. J. C. D.

Inorganic Chemistry.

Heat of Vaporisation of Hydrogen. W. H. Keesom (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1919, ii, 83; from *Chem. Zentr.*, 1920, i, 147).—Dewar has determined the heat of vaporisation of hydrogen to be 123*WE*; the author, however, gives the values 108·5—113·2, the greater probability of which is supported by theoretical considerations. H. W.

Crystallography of Ice. F. Rinne (*Ber. Verh. Sächs. Ges. Wiss., Math.-Nat. Kl.*, 1917, **69**, 57—62; from *Jahrb. Min.*, 1919, *Ref.* 25—27).—The *X*-ray photograph of ice on the basal plane shows dihexagonal symmetry with $a:c=1:1·678$, but does not decide whether the crystal is hemimorphic or not. Ice belongs to the magnesium type of the author's "isotypes" (A., 1916, ii, 29), of which a tabulated list is given. L. J. S.

Vapour Pressure of Solid Bromine. Teófilo Isnardi (*Ann. Physik*, 1920, [iv], **61**, 264—272).—The vapour pressure of solid bromine has been determined at 0°, −10·9°, −15·5°, and −21·1° by two methods: (1) a manometric method, and (2) by allowing the vapour of bromine at measured temperature to fill a globe of known volume, condensing and weighing the liquid. The values obtained are considerably higher than those determined by Ramsay and Young (T., 1886, **49**, 453), except in the case of the value at 0°, which lies very near to that of Ramsay and Young. The following values are obtained: 0°, 65·83 mm.; −10·9°, 35·37 mm.; −15·5°, 21·95 mm.; and −21·1°, 15·75 mm. Extrapolation of the vapour-pressure curve to −41·3° gives values which agree very closely with those obtained by Cuthbertson by his optical method (A., 1911, i, 582). The triple point is calculated to lie at −7·3° and 46·4 mm. pressure. The vapour pressure of solid bromine is given by the formula $\log p=a/T+b\log T+c$, where the constants have the values $a=-7109·142$, $b=-43·33195$, and $c=133·46929$. The heat of sublimation is calculated to 60·7 cal. per gram. J. F. S.

Revision of the Atomic Weight of Fluorine. E. Moles and T. Batuccas (*J. Chim. Phys.*, 1919, **17**, 537—588).—See this vol., i, 283.

Mass of the Litre of Air and Gas Mixtures. A. Leduc (*Engineering*, 1919, **108**, 569).—A résumé of the more important of the results published by Leduc (*Trav. Mem. Bureau Internat. Poids et Mesures*, **16**). Two gases, *A* and *B*, both at pressure *P* and of equal volume, when mixed in double the volume have not the same pressure as before mixing, but a pressure $P+\epsilon+\epsilon_1$, where ϵ and ϵ_1 depend on the nature of the gases. If the two gases are similar chemically, $(\epsilon+\epsilon_1)$ is immeasurable, as, for example, is the

case with a mixture of carbon dioxide and nitrous oxide, but in the case of hydrogen and sulphur dioxide the mixture has a pressure 3 mm. greater than the pressure of the constituents. As regards the mixture of oxygen and nitrogen in the atmosphere, ϵ may be disregarded. The density of air has been determined by direct weighing of air and from the weight of the constituent gases. Paris air has the following composition by volume (carbon dioxide and water vapour having been removed): oxygen, 0·2100; nitrogen, 0·7806; argon, 0·0094; neon, 15×10^{-6}; helium, 5×10^{-6}; hydrogen, 1×10^{-6}; krypton, 50×10^{-9}, and xenon, 6×10^{-9}; by weight: oxygen, 0·2321; nitrogen, 0·7549; argon, 0·0130; neon, $8·4 \times 10^{-6}$; helium, $0·7 \times 10^{-6}$; hydrogen, $0·07 \times 10^{-6}$; krypton, 140×10^{-9}; and xenon, 30×10^{-9}. The rare gases, with the exception of argon, only affect the density of air in the fifth decimal place. A litre of air at 0° and 760 mm. weighs 1·2928 grams when $g = 980·665$; under a pressure of 1 megabar, if g is 980·97 and the density of mercury is 13·5951, the weight is 1·2759 grams. Samples of air collected all over France and Algiers and at various altitudes show a weight percentage of oxygen varying between 23·05 and 23·25%. The oxygen percentage is lower in the north of France, and there is generally less oxygen close to the soil than at the height of foliage. J. F. S.

Equilibrium in the System Ammonia-Ammonium Thiocyanate. H. W. FOOTE and M. A. HUNTER (*J. Amer. Chem. Soc.*, 1920, **42**, 69—78).—With the object of finding an absorbent other than water for free ammonia, the system ammonia–ammonium thiocyanate has been investigated. The vapour pressure of ammonia–ammonium thiocyanate mixtures has been determined by passing ammonia at known pressure through a known weight of ammonium thiocyanate until no further increase in weight occurred; in this way the vapour pressure of ammonia is known. This was carried out at temperatures 0—40°. A further series of vapour-pressure measurements was made for saturated aqueous solutions of ammonia and ammonium thiocyanate at temperatures −78° to +20°, and the following values obtained: −78°, 1 mm.; −65°, 4 mm.; −50°, 9 mm.; −34°, 21 mm.; −23°, 34 mm.; −20°, 41 mm.; 0°, 107 mm.; and +20°, 225 mm. The solubility of ammonium thiocyanate in ammonia has been determined at temperatures from 0° to 50°, and the following composition of saturated solutions is obtained: 0°, 23·3% ammonia, 76·7% thiocyanate; 10°, 22·65% ammonia, 77·35% thiocyanate; 20°, 21·6% ammonia, 78·4% thiocyanate; 30°, 20·15% ammonia, 79·85% thiocyanate; 40°, 18·4% ammonia, 81·6% thiocyanate; 50°, 16·65% ammonia, 83·35% thiocyanate. The specific conductivity of several solutions at 0° has been measured and the following values obtained: 75 mol. % ammonia, 0·1979 ohms^{-1}; 68·9 mol. % ammonia, 0·1640 ohms^{-1}; 63·3 mol. % ammonia, 0·1395 ohms^{-1}; 59·7 mol. % ammonia, 0·1246 ohms^{-1}; and 57·1 mol. % ammonia, 0·1110 ohms^{-1}. The vapour pressures found are much lower than Raoult's law requires. The practical application of ammonium thiocyanate as an absorbent

for ammonia has been considered, and it is shown that such an absorbent could be used in cases where it is necessary to eliminate water, and that a very large amount of the ammonia (98·1—99·6%) would be easily recoverable. J. F. S.

Catalytic Oxidation of Ammonia to Nitric Acid. B. NEUMANN and H. ROSE (*Zeitsch. angew. Chem.*, 1920, **33**, 41—44, 45—48, 51—55).—The authors have summarised the numerous processes and research in connexion with the catalytic oxidation of ammonia, and contribute some further results of investigations. Highest yields are obtained with platinum at 500° (96%), ferric oxide at 670° (90%), and iron–bismuth oxide at 600° (95%). The influence of the ammonia concentration, of the velocity of the gases, and of the temperature is discussed. Curves are given for the gas composition with various catalysts between 300° and 700°. Under definite conditions the oxidation will proceed continuously without external heat. W. J. W.

Vapour Pressure of Arsenious Oxide in Sulphuric Acid Solutions. F. SCHWERS (*J. Soc. Chem. Ind.*, 1920, **39**, 33—34T).—In the contact process for the manufacture of sulphuric acid, the sulphur dioxide is washed by bubbling through sulphuric acid. Experiments were made to determine to what extent arsenious acid is removed from the sulphuric acid by the sulphur dioxide, since any appreciable amount so carried forward would have a serious poisoning effect on the catalyst. In the experiments a measured volume of air was bubbled through sulphuric acid at 60° containing a known amount of arsenious oxide, and was then passed through a series of sodium hydroxide absorption tubes to collect any volatilised arsenic. The acid used contained, in two experiments, 0·015% and 0·001% of arsenious acid, and in each case small but appreciable amounts of arsenic were found in the absorption tubes, the amount carried forward being proportional to the amount present in the acid, and more than sufficient to have a poisoning effect on the catalyst. E. H. R.

Atomic Weights of Boron and Fluorine. EDGAR F. SMITH and WALTER K. VAN HAAGEN (*Carnegie Inst. Pub.*, 1918, **267**, 1—63).—Methyl alcohol obtained by the hydrolysis of methyl oxalate was used to prepare methyl borate, from which boric acid was produced by hydrolysis. The acid thus obtained and sodium carbonate gave borax, which was completely dehydrated by prolonged fusion. The anhydrous borax, by treatment with the appropriate acid and repeated evaporation with methyl alcohol, was converted into sodium chloride, sulphate, nitrate, and carbonate, from the weights of which the atomic weight of boron was calculated. The anhydrous borax was also indirectly converted into sodium fluoride through the formate, the direct conversion being impracticable.

The values obtained are 10·900 for boron and 19·005 for fluorine.

The boron value is 1% lower than the accepted value, which is erroneous owing chiefly to the retention of water by borax glass.

CHEMICAL ABSTRACTS.

The Combustion of Wood Charcoal with Nitric Acid. FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 40).—Wood charcoal was heated in a current of nitric acid vapour and the resulting gases were collected and analysed. The gases had approximately the following composition: CO_2, 57·2%; CO, 13·3%; H_2, 4·6%; N_2, 24·9%. The high carbon monoxide content and the presence of free hydrogen are noteworthy. It was observed that a considerable quantity of ammonia was present in the condensate. The production of ammonia is difficult to account for, as the reaction temperature was at least 1000°. E. H. R.

Adiabatic Compression of Carbon Dioxide at High Temperatures. KURT NEUMANN (*Zeitsch. Ver. deut. Ing.*, 63, 1002—1007; from *Chem. Zentr.*, 1919, iii, 989).—The author has investigated the expansion of carbon dioxide which, enclosed in an insulated cylinder, had previously been heated to such a temperature that partial dissociation into carbon monoxide and oxygen had occurred (a phenomenon which is observed in internal combustion engines). During the expansion, combination of carbon monoxide and oxygen to carbon dioxide (after combustion) takes place, which has an important influence on the adiabatics. Expressions have been developed which permit the calculation of gaseous composition, pressure, and volume at a definite temperature. H. W.

Aqueous Solutions of Carbon Dioxide. ROBERT STROHECKER (*Inaug.-Diss. Marburg*, 44 pp.; from *Jahrb. Min.*, 1919, *Ref.* 1).—Carbon dioxide solutions are important agents in geological processes. The slow neutralisation of such solutions by various bases was investigated, with the idea of gaining some idea as to their constitution. It appears that carbonic acid is not such a weak acid as is generally supposed, the dissociation constant being much higher than is usually stated. The acid constant was determined as $k = 44 \cdot 10^{-5}$; it behaves, therefore, as an hydroxyformic acid.

L. J. S.

Fall in Pressure, Density, and Heat of Vaporisation of Argon. C. A. CROMMELIN (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1919, **11**, 81—83; from *Chem. Zentr.*, 1920, i, 147).—The latent heat of vaporisation of argon at −185·5° is found to be 69·4*WE*. Values for the fall in pressure and density at numerous temperatures are given in tabular form. H. W.

Surface Colours of Metals. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1919, 225—236; from *Chem. Zentr.*, 1920, i, 148).—Metals which yield surface colours become coated with a film of oxide, the rate of thickening of which with the time can be estimated by the alteration of the surface colours. Certain metals yield similar colours with iodine vapour at the ordinary tempera-

ture, and these are particularly suitable for the experimental investigation of the laws governing the rate of formation of the surface layer. The isothermal rate depends solely on the coefficient of diffusion of iodine into the layer of silver iodide covering the silver, and hence there is a parabolic dependence of thickness on time of action. The author's theory, which is confirmed by experiment, is based on the same fundamental ideas as Nernst's theory of solution. The actual chemical action occurs far more rapidly than the diffusion process, which, in the one case, leads to an attack of the reagent on the metal through a layer of constantly increasing thickness, whilst, in the other case, action occurs through a layer of constant thickness, since the deposit becomes detached. The quantitative relationships therefore depend on the different properties of the layers of reaction products. If crystals of iodine are placed in a desiccator over sulphuric acid, iodine vapour is observed which give surface colours with silver, copper, lead, and thallium; bismuth and antimony rapidly darken, and a fine, dark dust is deposited on their surfaces. Tin behaves similarly, but yields a yellow, incoherent layer. Small patches are formed within a few minutes on iron, cobalt, nickel, and manganese, and these, when removed from the desiccator, rapidly form droplets since the iodides are hygroscopic. Zinc and cadmium are more regularly, but much more slowly, attacked; with chromium, action is doubtful. With metals which give surface colours, the rate of increase of the layer which causes the coloration can be determined if care is taken to keep the concentration of iodine vapour constant. For this purpose air is drawn through a definite iodine solution, and the surface colour is compared at definite intervals with a table which gives the relationship between surface colour and thickness of film. A strip of silver shows three different types of behaviour towards iodine according to whether it has been rolled and cleaned, has been melted and thus covered with large crystallites, or has been left unworked and thus covered with multitudinous, small, dendritic crystals. The surface colorations on copper are similar to those on silver which has been similarly treated. Since, however, the index of refraction of copper iodide has not been determined, the thickness corresponding with the colours of the corresponding layers of air cannot be calculated to actual thicknesses of iodide film. In many regions of temperature, the rate of increase of the superficial layer is independent of the temperature; this is true in the case of steel, for which the author gives calculations based on Löwenherz's experiments. H. W.

Segregation Dispersoids in Anisotropic Media. WILHELM EITEL (*Centr. Min.*, 1919, 173—183).—When homogeneous mixtures of sodium and potassium chlorides are cooled rapidly from a high temperature, metastable, homogeneous mixed crystals can be obtained which, however, when maintained for some time at a suitable temperature, decompose into the constituent salts, the crystals becoming opaque. This phenomenon has been investigated by the

ultramicroscopic method used by Lorenz and Eitel for the examination of metallic fogs in crystals of the corresponding chlorides (A., 1915, ii, 260, 261). A complete series of mixtures of the two salts was examined, and it was shown that the segregation of the mixture can be optically demonstrated under the ultramicroscope through the gradual formation of a fog or fine dispersoid phase at a temperature of about 250°. A number of photographs are reproduced. E. H. R.

Solidification Points of Mixtures of Metallic Chlorides. FRED. C. A. H. LANTSBERRY and R. A. PAGE (*J. Soc. Chem. Ind.*, 1920, **39**, 37—41T).—The authors have determined the freezing-point curves of the three binary mixtures and one ternary mixture comprised in the system sodium chloride–potassium chloride–calcium chloride by the cooling method, that is, plotting the cooling curve of a mixture of known composition and noting the arrest point. In the sodium chloride–potassium chloride series the components form a continuous series of solid solutions; the lowest melting mixture contains 55% KCl and 45% NaCl, and solidifies at 650°. The curve for the sodium chloride–calcium chloride series shows a very sharp minimum at 72·5% $CaCl_2$ and 27·5% NaCl; the corresponding freezing point is 505°. The potassium chloride–calcium chloride series is more complicated. The curve shows two distinct eutectic points and a maximum between them at about 70% $CaCl_2$. The maximum corresponds with a freezing point of 725° and represents the formation of a compound, $2KCl,3CaCl_2$. The eutectic between the compound and $CaCl_2$ freezes at 608° and contains 17·5% KCl, whilst that between the compound and KCl freezes at 590° and contains 60% KCl. The results do not confirm the work of Menge (A., 1911, ii, 982), who reported the formation of a compound, $4NaCl,CaCl_2$, in the sodium chloride–calcium chloride series. Freezing-point determinations were made on a series of forty-one ternary mixtures, and the results are plotted on a triangular diagram in which the isothermal lines are shown. There are two ternary eutectics, one containing 70% $CaCl_2$, 25% NaCl, and 5% KCl. freezing at 495°, the lowest in the series, the other containing 30% $CaCl_2$, 20% NaCl, and 50% KCl, freezing at 530°.
E. H. R.

Additive Products of Sulphur Dioxide and Alkali Iodides (Alkali iodide Sulphones). FRITZ EPHRAIM (*Ber.*, 1920, **53**, [*B*], 118).—The alkali iodides absorb varying proportions of sulphur dioxide (A., 1916, ii, 614), whereas Forcrand and Taboury have recently stated that sulphones of the type $MI,3SO_2$ are produced (A., 1919, ii, 341). J. C. W.

The Dissociation of Ammonium Carbamate. C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1920, **170**, 462—464).—The values obtained by Naumann (this Journ., 1871, 1195) for the dis-

sociation pressures of ammonium carbamate over the temperature range $-15°$ to $+60°$ may be expressed by two equations:

$$\log p = -3{\cdot}635/T - 7{\cdot}045 \log T + 28{\cdot}692$$

and

$$\log p = -4{\cdot}821/T - 15{\cdot}4 \log T + 53{\cdot}3586.$$

Measurements made at 81° and 93°, where the pressures are several atmospheres, confirm the accuracy of these equations. Calculations made by means of these equations give the heat of dissociation of ammonium carbamate, at constant pressure, as $-39{\cdot}0$ cal., which is in close agreement with the value previously found by experiment (compare Matignon, A., 1908, ii, 465). W. G.

Growth Phenomena of Copper, Silver, and Gold. A. Beutell (*Centr. Min.*, 1919, 14—28).—When natural or artificial silver sulphide is heated in an evacuated sealed tube for several days at a temperature of 350—600° a certain amount of decomposition takes place. The small amount of silver formed seems to wander through the silver sulphide, appearing at the cooler end of the tube in the form of hair silver. A number of experiments which were made showed that neither silver foil nor hair silver is attacked by sulphur vapour in a vacuum at 450°; the metal remained bright after forty-eight hours. Silver foil heated alone in a vacuum for a long period at 450—585° showed no trace of the growth of hair silver, but when silver foil and silver sulphide were heated together at 450° remarkable growths were obtained in a comparatively short time. To obtain these growths it is necessary for the silver and the silver sulphide to be actually in contact. Similar growths of copper were obtained by heating together copper and cuprous sulphide, but the process was much slower. When silver selenide or telluride was used in place of the sulphide, similar growths of silver were obtained, and hair copper was obtained to a certain extent with copper selenide and telluride. With gold, the best results were obtained when gold telluride containing silver was heated with silver foil. After seven days' heating at 500°, growths of "moss" gold containing silver had appeared at the cooler end of the tube. E. H. R.

Action of Water on Strontium Sulphide. E. Terres and K. Brückner (*Zeitsch. Elektrochem.*, 1920, **26**, 25—32).—The action of water on strontium sulphide has been investigated. It is shown that the reaction in this case differs materially from the reaction in the case of barium sulphide (see following abstract). In the present case the reaction takes place between two molecules of water and two molecules of sulphide with the formation of equimolecular quantities of strontium hydroxide and strontium hydrosulphide: $2SrS + 2H_2O = Sr(SH)_2 + Sr(OH)_2$. The hydroxide and hydrosulphide, in consequence of their widely differing solubility, may be completely separated by crystallisation. When strontium sulphide is extracted with hot water and the clear filtrate cooled, pure strontium hydroxide crystallises. The solubility of strontium

hydrosulphide has been determined at temperatures 0—100°, and the following values obtained in grams of the anhydrous compound per 100 grams of water: 0°, 27·5; 20°, 29·7; 40°, 31·6; 60°, 33·2; 80°, 35·6; 100°, 37·8. The solubility of strontium hydroxide and strontium hydrosulphide in the same solution has been determined over the range 0—100°, and it is shown that no mixed compound is formed and that the hydroxide and hydrosulphide are in equilibrium with one another at all temperatures. Hence strontium hydroxide may be prepared by direct crystallisation of the solution obtained by the action of water on strontium sulphide. J. F. S.

Action of Water on Barium Sulphide. E. Terres and K. Brückner (*Zeitsch. Elektrochem.*, 1920, **26**, 1—24).—The conditions influencing the formation of barium hydroxide from barium sulphide are experimentally investigated. A long list of patents and investigations is given with short critical remarks. A number of processes are repeated which are based on the action of water on barium sulphide and in which the crystalline product is worked up to barium hydroxide either by crystallisation or by treatment with metallic oxides. The results confirm in many cases the published accounts. The concentration of the solution and the composition of the residue, obtained by extracting barium sulphide with water at various temperatures, are investigated. The content of the solution of barium hydroxide and barium hydrosulphide increases rapidly with increasing temperature. The solid residue consists to the extent of $\frac{1}{3}$—$\frac{1}{4}$ of barium oxide. The solutions contain equal molecular quantities of hydroxide and hydrosulphide, so that it would appear as though in the presence of one another these substances had the same solubility in water. The action of barium hydroxide solution on barium sulphide shows, however, that the solution is not saturated with barium hydroxide. Hence it would seem that the solution is saturated with an intermediate compound, either an hydroxyhydrosulphide or a double compound of barium hydroxide and barium hydrosulphide, but it is not saturated with the components of this double compound. The solubility of barium hydrosulphide is determined from $-15°$ to 100°. It is shown that the intermediate compound is formed when barium hydroxide and barium hydrosulphide are mixed in definite proportions, and that the maximum quantity of the compound is precipitated when twenty-seven molecules of the hydrosulphide are mixed with one molecule of the hydroxide; also the greater the excess of hydrosulphide the purer the precipitated double compound. The double compound may be expressed by one of the formulæ

$$OH\cdot Ba\cdot SH,5H_2O$$

or $Ba(OH)_2,Ba(SH)_2,10H_2O$. Experiments on the solubility of the intermediate compound show that the solution contains the components in very different proportions to the solid substance, that is, the undissolved residue contains an excess of hydroxide. The intermediate compound is shown to possess a considerable stability except towards oxidising agents, and there is no considerable decom-

position by water either with or without pressure or even by alkalis. The compound in relation to the hydrosulphide possesses a very small hydrogen sulphide pressure. For these and other reasons the author allots the formula $OH{\cdot}Ba{\cdot}SH,5H_2O$ to this compound. The solubility of barium hydroxide and barium hydrosulphide simultaneously has been determined from the cryohydric point to 100°. At all temperatures the region of existence of the double compound lies between those of barium hydroxide and barium hydrosulphide. The two simple compounds, therefore, can never exist together in the same solution, but must combine to form the intermediate product. It also follows that pure barium hydroxide can never be crystallised from the solution obtained by the action of water on barium sulphide. J. F. S.

Solubility of Zinc in Cyanide Solutions. H. A. White (*J. Chem. Met. Min. Soc. S. Africa*, 1919, **20**, 97—101).—From the results of an investigation made to determine the effect of various practical conditions on the solution of zinc during the precipitation of gold from cyanide solutions, it is concluded that close regulation of cyanide strength, alkalinity, and aeration of the auricyanide solution is necessary if the consumption of zinc is to be kept within reasonable limits. The ideal of a zinc consumption corresponding even approximately with the amount of gold precipitated appears unlikely to be attained. [For further details, see *J. Soc. Chem. Ind.*, 1920, April.] W. E. F. P.

Attempt to Determine if Common Lead could be Separated into Isotopes by Centrifuging in the Liquid State. J. Joly and J. H. J. Poole (*Phil. Mag.*, 1920, [vi], **39**, 372—375). —Molten lead has been centrifuged at a rate of 9000 revolutions per minute in electrically heated steel tubes for periods of one hour. The top and bottom layers were then withdrawn and cast into pellets, and the density determined. Although small differences between the density of the two layers are observed, they lie inside the experimental error, so that the experiments furnish no evidence that a separation of the isotopes has been effected.

J. F. S.

Effect of Centrifuging certain Alloys while in the Liquid State. J. Joly and J. H. J. Poole (*Phil. Mag.*, 1920, [vi], **39**, 376).—Using the method described above (see preceding abstract), it is found that silver–lead alloys could not be appreciably separated by centrifuging, but lead–tin alloys could be to some extent separated. Thus with an alloy containing 82% of lead and 18% of tin the top layer was 1·8% lighter than the bottom layer after centrifuging. J. F. S.

The Action of Water on Lead. J. F. Liversedge and A. W. Knapp (*J. Soc. Chem. Ind.*, 1920, **39**, 27—33T).—The experiments here recorded on the action of water on lead were made with the waters collected in the Caban reservoir, Elan Valley, Wales, for

the use of Birmingham. These waters have a slight alkalinity, due to hydrogen carbonates, etc., equal to about 0·3 part $CaCO_3$ per 100,000. The action of such waters, and generally of waters the alkalinity of which does not exceed 1·5, is erosive. The whole surface of the lead is attacked and a flocculent precipitate forms, which, becoming detached, leaves the surface of the lead bright but mottled. When the alkalinity is increased to 1·5—2·5 the action becomes corrosive, and a loosely-held, white, opaque crust forms here and there on the surface. With still greater alkalinity the lead almost invariably becomes covered with a dull white film, which appears to act as a protective coating. The erosion tests were made by the method of Houston, in which a clean strip of lead of standard size is immersed in the water in a test-tube, air having free access. The amount of lead eroded is determined colorimetrically as sulphide. It proved possible to carry out the test in one day. It was found that such variations as occurred naturally in the amount of oxygen present in the water had no appreciable effect on the erosion. Variations in the amount of water used did not affect the amount of erosion, but the greater the depth of immersion of the lead the smaller was the velocity of attack. Exposure to glass lowered the erosive ability of the water. Erosion readily occurred in waters free from carbon dioxide, and small variations in the carbon dioxide content had no appreciable effect. The presence, however, of from 1 to 2% of carbon dioxide by volume caused a sudden change from erosion to "plumbo-solvency," that is, the lead precipitate no longer appears but soluble lead hydrogen carbonate is formed. Carbon dioxide dissolves lead more rapidly in presence of oxygen than alone. It is concluded that, given oxygen present, the principal factor in determining both amount and kind of erosion is the alkalinity of the water. The addition of small quantities of calcium hydroxide, carbonate, or hydrogen carbonate or of potassium permanganate decreases erosion, but calcium hydrogen carbonate is most effective; erosion occurs in absence of bacteria. It was observed that the bacteria in the water are not all destroyed by exposure to lead for six hours. E. H. R.

The Alloys of Copper, Zinc, and Nickel. Léon Guillet (*Compt. rend.*, 1920, **170**, 460—462).—Brasses containing nickel, in which the copper content falls to 40% and even less and the nickel content rises to 15%, are of particular interest because of their mechanical properties. Their breaking strain varies from 45 to 75 kilos./mm.^{2} with elongations of 45—18%. They are readily malleable at high temperatures, and in colour and resistance to oxidation they are comparable to German silver. W. G.

Compressibility of Indium. Theodore W. Richards and Jitsusaburo Sameshima (*J. Amer. Chem. Soc.*, 1920, **46**, 49—54). —The compressibility of indium has been determined over the pressure range 100—500 megabars. The measurements were made

at 25°. At this temperature indium has a density 7·318. The measurements were carried out by the usual method, but instead of a steel piezometer, as previously used, a small glass one was made use of in the present work. It is found that the compressibility of indium over the range examined is 0·0000027, or about two-thirds that of mercury. J. F. S.

The Limits of the Combining Power of Silicon with certain Metals of the Iron Group. A. SANFOURCHE (*Rev. Mét.*, 1919, **16**, 239—245; from *Chem. Zentr.*, 1920, i, 149—150).—The uncertainties in the literature concerning the combining power of silicon with members of the iron group are frequently to be ascribed to faulty methods of analysis consisting in the treatment of the alloy with alkaline reagents to effect removal of the excess of silicon and isolation of the alloy richest in silicon from the residue. Actually, the persilicated compounds are frequently attacked in the circumstances, whilst removal of the free silicon enclosed in the alloy is frequently incomplete. In addition, the combining power of silicon with iron and related substances is not a constant quantity, but depends on various factors, notably on the excess of free silicon. In ferrosilicons, the lower limit of combining power lies at 55·55% Si, corresponding with the formula Fe_2Si_5, the upper limit at 60% Si corresponding with $FeSi_3$. With manganese–silicon alloys the limit lies between 46·70 and 50·11% Si; the upper value is here obtained with 8% of free silicon, whilst for iron, in similar circumstances, a 2% excess of silicon suffices. The higher limit approximates to the formula $MnSi_2$, so that this compound may be regarded as having the highest possible silicon content; the lower limit does not correspond with a definite compound, whilst the substance $MnSi_2$ appears to require the presence of a sufficient excess of silicon to prevent its dissociation with liberation of this element. The influence of silicon is also very noticeable with cobalt silicon alloys; as it increases from 0% to 6% the combining power increases from 50% to about 53%. Neither limit corresponds with a definite chemical compound; the simple formulæ to which they most closely approximate are $CoSi_2$ (48·7% Si) and Co_2Si_5 (54·26% Si). With nickel–silicon alloys the limits of combining power are most widely separated (39—45%); in this case also a definite compound is not indicated. The upper limit is only attained in the presence of at least a 10% excess of free silicon.

The method of analysis consists in the estimation of total silicon by treatment with alkali carbonate and of uncombined silicon by removal of the combined element as silicon tetrafluoride by treatment with pure hydrofluoric acid. Combined silicon is estimated by difference.

The author is led to the conclusion that compounds of the iron group rich in silicon tend to dissociate partly into free silicon and a more or less well-defined compound of silicon and the metal: $M_xSi_y \rightleftharpoons M_xSi_{y-z} + Si_z$. Stabilisation occurs in the presence of a sufficient excess of silicon, but, if this is present in quantity only

sufficient to form the compound, a certain amount of it passes into the free condition (in solution) and so depresses the combining power. H. W.

Form of Ultra-microscopic Platinum Particle. RICHARD GANS and RICARDO CALATRONI (*Ann. Physik*, 1920, [iv], **61**, 465—470).—Using platinum sols prepared both by the Bredig process and by reduction of chloroplatinic acid with hydrazine hydrate in the presence of the sodium salt of protalbic acid as protecting colloid, the authors have measured the absorption for the four helium lines λλ 6678, 5877, 5010, and 4472 Å. units. To ensure uniformity of the particles and to remove aggregates, the solutions were filtered through collodion ultra-filters which contained 0·5—1·0% of acetic acid. The results show that as in the case of silver and gold amicrons (A., 1912, ii, 508; 1915, ii, 390), the platinum amicrons are spherical in form (see also Diesselhorst and Freundlich, *Physikal. Zeitsch.*, 1916, **17**, 117). J. F. S.

Mineralogical Chemistry.

The Composition of Coal. The Behaviour of the Constituents of Banded Bituminous Coal on Coking. RUDOLF LESSING (T., 1920, **117**, 247—256).

The Composition of Coal. The Mineral Constituents of Banded Bituminous Coal. RUDOLF LESSING (T., 1920, **117**, 256—265).

Villamaninite, a New Mineral. W. R. SCHOELLER and A. R. POWELL (*Min. Mag.*, 1920, **19**, 14—18).—As black, crystalline grains and small nodules, this occurs disseminated plentifully in a matrix of white, crystalline dolomite, which contains also some iron-pyrites, copper-pyrites, and quartz. It is from the Carmenes mines, near Villamanin, prov. Leon, Spain. Material isolated by dissolving away the dolomite matrix is seen to consist of small groups of rough crystals which show the forms of the cube and octahedron. The cube faces show a peculiar rounding, and it is these faces that form the bright convex and concave surfaces of the nodules. These nodules, never more than sectors of spheres, are due to the subparallel aggregation of crystals. The colour is iron-black with dull metallic lustre, and the streak is sooty-black; $H=4\frac{1}{2}$. The mineral is soluble in nitric acid, leaving a globule of sulphur. Heated in a bulb-tube it gives a sublimate of sulphur and selenium, and it burns in the air with a blue flame. Analysis I is of hand-picked, nodular material; II, of acid-cleaned nodular;

III, acid-cleaned crystalline; and IV, of acid-cleaned unsorted. Also traces of arsenic, bismuth, lead, and zinc:

	S.	Se.	Cu.	Ni.	Co.	Fe.	SiO_2.	Total.	Sp. gr.
I.	49·00	1·54	17·65	18·19	7·45	4·39	0·88	99·10	—
II.	49·13	1·44	18·51	18·24	7·24	4·17	0·34	99·07	4·433
III.	49·63	0·88	22·13	15·94	6·30	5·11	0·22	100·21	4·523
IV.	47·27	0·88	19·48	15·53	6·79	6·00	3·80	99·75	—

The atomic ratios $(S+Se):(Cu+Ni+Co+Fe)=1·953$, 1·936, and 1·904 for analyses I, II, and III respectively, approximating to the disulphide formula, $(Cu,Ni,Co,Fe)(S,Se)_2$. The presence of copper, nickel, and cobalt in a disulphide is discussed. L. J. S.

The Structure and Symmetry of Anatase, Rutile, Zircon, and Xenotime. A. JOHNSEN (*Centr. Min.*, 1919, 97—105).—Crystals of these minerals have been investigated by the *X*-ray method by Vegard (A., 1916, ii, 405, 593), who came to definite conclusions regarding their inner structure. Vegard's structures have been critically examined by the author, who finds that, whilst those of anatase, rutile, and xenotime are tetragonal holohedral, that of zircon must belong either to the hemimorphous hemihedral or to the hemimorphous tetartohedral class. Experiments on the pyro- and piezo-electric properties of crystals of zircon are desirable to test the point. E. H. R.

Dolomite from Leogang, Salzburg. O. GROSSPIETSCH (*Tsch. Min. Mitt.*, 1917, **34**, 68—70; from *Jahrb. Min.*, 1919, Ref. 274).—Blackish-grey crystals with the form of acute rhombohedra gave:

(CO_2 + trace of S).	FeO.	CaO.	MgO.	Total.	Sp. gr.
47·53	1·63	29·66	21·18	100·00	2·889

The sulphur is due to admixed pyrites. L. J. S.

A Singly Refracting Potassium Aluminium Sulphate of the Alunite Group. E. RAMANN and A. SPENGEL (*Centr. Min.*, 1919, 35—37).—Among the decomposition products of the rocks of the Solfatara di Puzzuoli, Naples, has been found a potassium aluminium sulphate having the composition

$$K_2O,3Al_2O_3,4SO_4,6H_2O.$$

It seems to have been formed by the action of sulphuric acid on the volcanic rock, and occurs, mixed with sulphur and silica, in the form of very fine particles, 0·001 to 0·002 mm. in diameter. It is singly refracting, but whether it is amorphous or belongs to the regular system it is difficult to say on account of the small size and rounded form of the particles. E. H. R.

Brannerite, a New Uranium Mineral. FRANK L. HESS and ROGER C. WELLS (*J. Franklin Inst.*, 1920, **189**, 225—237).—This is found as grains and rough prisms (tetragonal or orthorhombic?) in gold placers in Stanley Basin, central Idaho. The fragments

have a thin, brownish-yellow crust, but inside the material is brilliant black with conchoidal fracture. Opaque; streak, dark greenish-brown; H, $4\frac{1}{2}$. Thin splinters transmit yellowish-green light, and are optically isotropic; $n_{Li} = 2{\cdot}26$, $n_{Na} = 2{\cdot}30 \pm 0{\cdot}02$; D 4·5—5·43; fragments of higher density are more strongly radioactive. The mineral is slowly decomposed by concentrated sulphuric acid and by hydrofluoric and sulphuric acids. For the analysis it was fused with hydrogen sodium sulphate. Details are given of the method of analysis; titanium and uranium were separated by hydrolysis. In determining the state of oxidation of the uranium, the iron was assumed to be all ferrous, and this introduces a difficulty in deducing a formula. Other determinations of iron gave on unselected material Fe_2O_3 3·7%, and on the best selected material Fe_2O_3 3·0 or FeO 2·7%. The least radioactive material contained TiO_2 35·0%. Analysis by R. C. Wells (also traces Fe_2O_3, Al_2O_3, P_2O_5):

SiO_2.	TiO_2.	FeO.	CaO.	UO_2.	UO_3.	ThO_2.	Ce_2O_3.	Yt_2O_3, etc.
0·6	39·0	2·9	2·9	10·3	33·5	4·1	nil	3·9

ZrO_2.	PbO.	BaO.	SrO.	H_2O.	CO_2.	Total.	Sp.gr.
0·2	0·2	0·3	0·1	2·0	0·2	100·2	5·42

This analysis gives the ratios 9RO, Yt_2O_3, $5RO_2$, $11UO_3$, $46TiO_2$, $10H_2O$. Written as a metatitanate, the formula is

$$6(Ca,Fe,UO,TiO)TiO_3+8(Th,Zr,UO)Ti_2O_6+Yt_2Ti_3O_9+3H_2O.$$

Many analyses of complex uranium minerals are tabulated. Brannerite contains more uranium than any, with the exception of pitchblende. It appears to be nearest delorenzite (A., 1908, ii, 604), but contains less titanium and rare earths. L. J. S.

Crystal Structures of Wulfenite and Scheelite. Roscoe G. Dickinson (*J. Amer. Chem. Soc.*, 1920, **42**, 85—93).—The X-ray spectra of several planes of wulfenite ($PbMoO_4$) and scheelite ($CaWO_4$) have been measured and tabulated. For wulfenite the following values of n and $\sin\frac{1}{2}\phi_n$ are obtained, together with the intensities I, plane 101: $n=1$, $\sin\frac{1}{2}\phi_n=0{\cdot}0915$, $I=100$; $n=2$, $\sin\frac{1}{2}\phi_n=0{\cdot}1828$, $I=66$; $n=3$, $\sin\frac{1}{2}\phi_n=0{\cdot}2754$, $I=30$; $n=4$, $\sin\frac{1}{2}\phi_n=0{\cdot}3657$, $I=13$; and $n=5$, $\sin\frac{1}{2}\phi_n=0{\cdot}4553$, $I=5$. Measurements are also made for the planes 100, 110, 001, 111, and 102. In the case of scheelite two sets of values were obtained, using different specimens, plane 101: $n=1$, $\sin\frac{1}{2}\phi_n=0{\cdot}0950$, $I=100$; $n=2$, $\sin\frac{1}{2}\phi_n=0{\cdot}1905$, $I=59$; $n=3$, $\sin\frac{1}{2}\phi_n=0{\cdot}2860$, $I=18$; $n=4$, $\sin\frac{1}{2}\phi_n=0{\cdot}3805$, $I=8$. The planes 100, 110, 001, and 111 were also measured. It is shown that the face-centred lattice, with atoms so located as to form a diamond arrangement, accounts in each case for the relative spacings of different planes, and for the density of the crystals. The arrangement of the heavier atoms relative to one another has been determined by a qualitative consideration of the relative intensities. The difficulties in the location of the oxygen atoms are discussed. J. F. S.

[Composition] of Davidite. W. T. COOKE (*Trans. R. Soc. South Australia*, 1916, **40**, 267).—Material from Radium Hill, near Olary, South Australia, gave:

TiO_2.	FeO.	Fe_2O_3.	Ce_2O_3, etc.	U_3O_8.	CaO.	MgO.	PbO.	H_2O.	Total.
54·3	16·0	13·0	8·3	4·6	1·5	0·6	1·1	1·5	100·9

The cerium earths include much Ce, little Th, also La, Di, Er, Yt. Also some V_2O_5 and Cr_2O_3, included with the uranium oxide, trace of copper, and scandium detected spectroscopically. At a red-heat 100 grams of the mineral yielded about 15 c.c. of fairly pure helium. D. MAWSON in a preceding paper (*loc. cit.*, 262—266) describes the mode of occurrence of the mineral, and states it to be homogeneous (compare A., 1910, ii, 309). L. J. S.

Siliceous Sinter from Lustleigh, Devon. A. B. EDGE (*Min. Mag.*, 1920, **19**, 10—13).—Lodes traversing granite and containing a soft and powdery, micaceous hæmatite are worked at the Plumley mine. In one lode, however, this mineral is present as larger scales, and it is cemented into a hard, stony mass by siliceous sinter, which contains also crystals of fluor-apatite, tourmaline, and quartz. The sinter is hard and compact, but very fragile. It ranges in colour from almost pure white to blood-red, with rippled and folded bands of colouring. Analysis of pale red material gave (also CaO, P_2O_5, traces):

SiO_2.	Al_2O_3.	Fe_2O_3.	Na_2O.	K_2O.	H_2O at 105°.	H_2O >105°.	Total.	Sp. gr.
69·76	2·68	5·38	0·36	0·76	18·62	2·38	99·94	1·73

The origin of the material is discussed; it was evidently deposited as a silica jelly. L. J. S.

Hemimorphite on Fossil Bones from Broken Hill, Rhodesia. H. BUTTGENBACH (*Ann. Soc. Géol. Belgique*, 1919, **42**, *Congo Annexe*, 5—14).—Limb bones of mammals from the cave at Broken Hill mine (A., 1908, ii, 397) show (1) compact tissue consisting of calcium phosphate and carbonate with a trace of fluorine, but no chlorine or zinc; (2) a glistening, crystalline crust (anal. I) of hemimorphite coating the compact tissue externally and internally; (3) a spongy aggregate (anal. II) of minute crystals of willemite, smithsonite, hemimorphite, hopeite, parahopeite, and tarbuttite occupying the central cavity.

	ZnO.	Fe_2O_3, Al_2O_3.	CaO.	SiO_2.	P_2O_5.	Ign.	Total.
I.	63·10	1·22	1·68	22·88	1·38	9·30	99·56
II.	45·50	0·82	15·24	15·00	12·75	10·22	99·53

L. J. S.

[Halloysite from Worms Heath, Croydon, Surrey.] GEORGE MACDONALD DAVIES (*Quart. J. Geol. Soc.*, 1920, **75** [for 1919], 22—28).—A petrographical description is given of the

materials (clay, sand, and pebbles) filling large, vertic[illegible]s in the chalk at this locality. A white, clay-like materia[illegible]d in the sand in these pipes, and previously referred to allophane, is proved by the following analysis, by A. B. EDGE, to be halloysite. Formula, $Al_2O_3,2SiO_2,2H_2O+Aq$. Also traces of Na_2O and K_2O. D 2·44; n near 1·552. (After ignition, D 2·46 or 2·47; n about 1·542.)

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	H_2O (at 100°)	H_2O (100–250°).	H_2O (ign.).	CO_2.	Total.
41·88	36·26	0·30	0·23	7·71	0·85	13·06	0·17	100·46

L. J. S.

The Scapolites. NILS SUNDIUS (*Bull. Geol. Inst. Univ. Upsala*, 1918, **16**, 96—106; from *Jahrb. Min.*, 1919, *Ref.* 140—142).—Supplements previous work (A., 1919, ii, 163). An analysis by Mauzelius (1917) of scapolite from gabbro at Nautanen, Lapland, D 2·698, is calculated as marialite 29·17, sulphate-marialite 9·38, carbonate-meionite 61·46%, and the mineral has the refractive indices ω 1·575, ϵ 1·552. The composition of carbonate-marialite is now written as $NaHCO_3,3NaAlSi_3O_8$, and of sulphate-marialite as $NaHSO_4,3NaAlSi_3O_8$. Scapolite from lime-silica gneiss in the Gula valley, Trondjem, Norway, gave analysis I (Na_2O,H_2O not determined), corresponding with marialite 6, carbonate-marialite 31, carbonate-meionite 63; it has ω 1·585, ϵ 1·551.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Cl.	SO_3.	CO_2.	Total.
I.	48·87	27·55	0·62	15·65	0·18	0·24	—	4·16	97·27

In scapolite from the Laacher See, a redetermination of carbon dioxide in the original material analysed by Brauns (anal. I, A., 1917, ii, 325) gave 3·23% (as against 0·65%), corresponding with marialite 13, sulphate-marialite 10, sulphate-meionite 9, carbonate-meionite 68%; this has ω_{Na} 1·5901, ϵ_{Na} 1·5600. Another, also described by Brauns in 1914, contains CO_2 3·52% (rather than 0·26%), corresponding with marialite 6, carbonate-marialite 31, carbonate-meionite 63, and has $\omega-\epsilon=0·0284$. In their optical constants, these sulphate-rich scapolites do not differ from the carbonate-scapolites, and they fall into the same series.

L. J. S.

Prehnite from the Tatra Mountains. W. PAWLICA (*Bull. Acad. Sci. Cracow*, [*A*], 1916, 54—59; from *Jahrb. Min.*, 1919, *Ref.* 275—276).—Massive, white prehnite with associated epidote, albite, and calcite fills veinlets in oligoclase-biotite-granite on the Mengesdorf peak. In the vicinity of these veins the granite is much decomposed, suggesting that the minerals were deposited by hydrothermal processes. Cavities in the massive mineral are lined with

smal[redacted]s of prehnite. The mean of two analyses is (also traces of M[redacted]gO, K_2O, Na_2O):

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	H_2O at 110°.	H_2O >110°.	Total.	Sp.gr.
43·89	23·85	1·56	0·28	25·83	0·23	4·52	100·16	2·904

The prehnite is in places altered to a powdery aggregate of sericite scales and quartz grains, being sometimes represented as pseudomorphs. This alteration is expressed as follows:

$$3H_2Ca_2Al_2Si_3O_{12}\,(\text{prehnite}) + K_2CO_3 + 6H_2CO_3 =$$
$$2H_2KAl_3Si_3O_{12}\,(\text{sericite}) + 3SiO_2\,(\text{quartz}) + 6CaCO_3 + H_2CO_3 + 6HO_2.$$

L. J. S.

A New Description of Amesite. EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **49**, 96—98).—A specimen from the disused emery mine at Chester, Massachusetts, shows hexagonal plates 1 cm. across of pale bluish-green amesite, with associated diaspore, magnetite, and rutile. The basal cleavage is not so perfect as in most other chlorites; H $2\frac{1}{4}$, D 2·77. The crystals are optically positive and biaxial, but with very small axial angle; $\alpha=\beta=1{\cdot}597$, $\gamma=1{\cdot}612$. Before the blowpipe, the mineral swells and exfoliates slightly, becoming silvery brownish-white in colour. It is partly decomposed by boiling sulphuric, nitric, or hydrochloric acid, with separation of flocculent silica. Most of the water is lost at only a dull red heat. Analysis:

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	MnO.	H_2O >110°.	H_2O >110°.	Total.
20·95	35·21	8·28	0·58	22·88	trace	0·23	13·02	101·15

agrees with the formula given by Pisani in 1876, namely,

$$H_4(Mg,Fe)_2Al_2SiO_9,$$

except for the ratio MgO : FeO, which is here =5 : 1. This formula was adopted by Tschermak in 1890 for a fundamental end-member of the chlorite group. L. J. S.

Optical Characters of the Olivine Group. H. MAGNUSSON (*Geol. För. Förh.*, 1918, **40**, 601—626; from *Jahrb. Min.*, 1919, *Ref.* 277—279).—Previous attempts at the correlation of the optical constants and the chemical composition of the members of the olivine group (A., 1911, ii, 616) have been confined to the series Mg_2SiO_4–Fe_2SiO_4 (forsterite-fayalite). This is now done for the series Mg_2SiO_4–Mn_2SiO_4 (forsterite-tephroite) and Mn_2SiO_4–Fe_2SiO_4 (tephroite-fayalite). Previously published results, supplemented by some new optical determinations, are tabulated and plotted. Passing along the linear series Mg_2SiO_4–Mn_2SiO_4–Fe_2SiO_4, there is a gradual diminution in the optic axial angle and an increase in the refractive indices, but the latter, when plotted against the composition, do not lie along a straight line.

L. J. S.

Belgian Minerals. H. Buttgenbach (*Ann. Soc.* [redacted]*ue*, 1919, **42**, *Mém.* 93—124).—Crystallographic and [redacted]terminations were made on hopeite, apophyllite, hemimorphite, barytes, anglesite, lepidolite, fuchsite, aragonite, gypsum, and calcite from various localities in Belgium. A brown clay, from Furfooz, with waxy lustre, easily breaking into irregular fragments with conchoidal fracture, unctuous, and adhering to the tongue, has H a little more than 2 and D 2·05. Before the blowpipe it decrepitates, and in the closed tube gives off water and blackens. In water, it breaks up with a slight noise and slowly falls to powder, but does not make a paste. It is, in part, soluble in acids. These characters, as well as the following analysis, point to bole.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	P_2O_5.	Ign.	Total.
38·67	27·13	11·25	1·15	1·10	1·34	19·34	99·98

The portion (24·21%) soluble in acids contains Al_2O_3 7·67 and Fe_2O_3 9·36%. Deducting these as bauxite ($Al_2O_3,2H_2O$) and limonite, the remainder corresponds in composition with a mixture of halloysite and opal.

A whitish efflorescence on the coal shale of the Bois-l'Evêque colliery, near Liége, is found on optical examination to consist mainly of trona ($3Na_2O,4CO_2,5H_2O$). Recalculating an old analysis (Malaise, 1881) of this material and deducting the sulphate as thenardite or as mirabilite, gives, however, a remainder with the composition $3Na_2O,3CO_2,13H_2O$ or $3Na_2O,3CO_2,11H_2O$.

L. J. S.

The Richardton Meteorite. T. T. Quirke (*J. Geol.*, 1919, **27**, 431—449).—This meteorite belongs to the veined spherical chondrite class (Cca) of Brezina's classification. Under the microscope these stones reveal a composition of olivine, monoclinic pyroxene, glass, metallic iron, and troilite. A notable characteristic is the veining. The veins are not continuous, and consist largely of troilite and metallic iron and nickel. In most cases the metal and sulphide are mingled in a manner to suggest contemporaneous deposition or concentration. A few specks of metallic copper were noted in the troilite. An analysis showed: metallic portion 19·90%, silicate portion 80·10%. The metallic portion gave: Fe 90·89, Ni 8·92, Co 0·15, P 0·04%. The silicate portion yielded: SiO_2 44·49, TiO_2 0·10, Al_2O_3 2·46, Cr_2O_3 0·64, Fe_2O_3 4·34, P_2O_5 none, MnO 0·19, FeO 16·23, CaO 2·69, MgO 28·32, Na_2O 0·85, K_2O 0·165%. These analyses were made from fragments representative of the matrix, and not on the vein material. It is estimated that about 90 kilos. of material have been recovered, the largest single piece weighing 8·7 kilos.

Chemical Abstracts.

Analytical Chemistry.

A Cheap Substitute for Platinum Wire for Flame Tests. A. EHRINGHAUS (*Centr. Min.*, 1919, 192).—The platinum wire used for carrying out flame tests can be simply and cheaply replaced by a strip of filter paper. To test a solution, a strip of pure filter paper is folded several times, and one end dipped in the solution. The damp end is then held in the outer flame of a Bunsen burner. If an insoluble salt is to be tested, the strip is first dipped in dilute hydrochloric acid, and a little of the salt is then sprinkled on the damp end. In either case, a good, pure flame coloration is obtained, which lasts as long as the paper is prevented from burning by the moisture or the salt. A lasting, monochromatic flame can be obtained by dipping one end of a strip of paper in a vessel containing the dissolved salt, the other end being held in the Bunsen flame. The paper is prevented from burning by a crust of salt, which soon forms. E. H. R.

Use of certain Indicators. Sensitised Sodium Alizarinsulphonate. W. MESTREZAT (*J. Pharm. Chim.*, 1920 [vii], **21**, 185—192).—Sensitised sodium alizarinsulphonate (prepared by neutralising the commercial product, which is nearly always alkaline in reaction) is a sensitive indicator for use in the titration of mineral acids, oxalic acid, and alkali hydroxides, and possesses the advantage over phenolphthalein and litmus that it can be used for the titration of both ammonia and phosphoric acid; it cannot, however, be used in the presence of carbonates. W. P. S.

Modified Orsat Apparatus. THOS. B. SMITH (*Gas World*, 1919, **71**, 379).—The gaseous mixture is passed under the maximal pressure of the reservoir through a platinum capillary tube, 13 cm. long and 1·6 mm. in external diameter, which is raised to a white heat, into an additional absorption pipette filled with water. The mixture is thrice returned and re-passed through the capillary, whereby combustible gases are completely burnt. The resultant mixture of carbon dioxide, oxygen, and nitrogen is analysed in the usual manner. CHEMICAL ABSTRACTS.

Improved Method of, and Apparatus for, Detecting Water Vapour or either of the Gaseous Components thereof. HENRY EDWARD FANE GOOLD-ADAMS, WILLIAM HENRY BOUSFIELD, and GEORGE WILLIAM TODD (Brit. Pat. 137547).—The gases suspected of containing water vapour, or either oxygen or hydrogen, which must first be converted into water by passing over a suitable catalyst, are passed over a salt, such as an alkali chloride or nitrate, which forms part of an electric circuit. If the partial pressure of the water vapour exceeds the critical hydration pressure of the particular salt

selected, it takes up moisture and allows a current [redacted] the circuit, whereby a suitable indication may be given [redacted] of a galvanometer or an electric bell operated by a relay. The salt is conveniently placed between a pair of wire gauze electrodes, through which the gases are passed. The device is particularly applicable in cases where it is necessary to provide against an explosive mixture of oxygen and hydrogen in gaseous reactions, such as in the synthetic production of ammonia, in which cases a continuous sampling of the mixed gases is secured by means of a by-pass, and a salt is selected of which the hydration pressure is approximately equal to the partial pressure of the aqueous vapour corresponding with the percentage of oxygen, against which a warning is required. G. F. M.

Short Modification of the Official Method of Estimating Chlorine in Foods, Fæces, and Urine. J. O. Halverson and E. B. Wells (*J. Biol. Chem.*, 1920, **41**, 205–208).—The complete washing out of the excess of silver nitrate from the silver chloride precipitate is eliminated, and, instead, an aliquot portion of the direct filtrate is titrated with ammonium thiocyanate. It is recommended that the reagents for titration be 0·05*N*.

J. C. D.

The Oxidation-potentiometric Titration of Iodides in the Presence of Chlorides and Bromides. I. M. Kolthoff (*Rec. trav. chim.*, 1920, **39**, 208—214).—Using the method of titration previously described (A., 1919, ii, 352), iodides may be estimated in the presence of any quantity of chlorides or of relatively large amounts of bromides, by titration with potassium dichromate, or, preferably, potassium bromate or iodate, the titration being carried out in the presence of hydrochloric acid.

W. G.

Estimation of Oxygen by the Copper-Ammonia-Ammonium Chloride Reagent. W. L. Badger (*J. Ind. Eng. Chem.*, 1920, **12**, [2], 161—164).—Hempel's method for the absorption of oxygen by means of metallic copper spirals covered with a solution containing equal parts of saturated ammonium carbonate solution and ammonia (D 0·93) was the basis for a series of experiments in which varying strengths of ammonia, and salts of ammonia other than the carbonate, were used. The results were compared by determining in each case the specific absorption as defined by Anderson. Specific absorptions were found of 22·5 vols. with a concentrated ammonia solution (D 0·90) saturated with ammonium chloride, 45—47 vols. with a mixture of two parts of concentrated ammonia and one of water saturated with ammonium chloride, 55—60 vols. with a mixture of one part of concentrated ammonia and one of water saturated with ammonium chloride, and 30 vols. with a mixture of one part of concentrated ammonia and two of water saturated with ammonium

chl[illegible] author concludes that an improvement on Hempel's meth[illegible]ained by using a solution prepared by saturating a mixture [illegible] one part of concentrated ammonia and one of water with ammonium chloride. This solution may be used to absorb fifty to sixty times its volume of oxygen, after which, although its absorption capacity is not exhausted, the amount of precipitate formed makes the solution unworkable. It is claimed that this reagent is cleaner and has a longer life than alkaline pyrogallol; unlike phosphorus, it is unaffected by catalysts, is readily prepared, and is active at almost any temperature. On the other hand, it cannot be used for mixtures containing carbon monoxide or acetylene, and when fresh it is liable to leave measurable amounts of ammonia in the gas. S. S. A.

The Estimation of Nitrogen in Nitrocellulose and Inorganic Nitrates with the Nitrometer. Ernest George Beckett (T., 1920, **117**, 220—235).

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. A. Stutzer (*Landw. Versuchs. Stat.*, 1919, **94**, 251—264).—Conditions are given under which phosphoric acid may be estimated by precipitating it as ammonium phosphomolybdate and weighing the precipitate directly. The precipitation is made in a nitric acid solution containing a small quantity of sulphuric acid, and the precipitate, after being collected on a weighed asbestos filter, is washed first with 2% ammonium nitrate solution, then with alcohol or acetone, dried at 100° for one hour, and weighed. The weight of the precipitate is multiplied by 0·03513 to obtain the amount of P_2O_5. [See, further, *J. Soc. Chem. Ind.*, 1920, 250A.] W. P. S.

Estimation of Arsenic in Organic Compounds such as Salvarsan. L. Joslyn Rogers (*Can. Chem. J.*, 1919, **3**, 398).—The sample, 0·5 gram, dissolved in 10 c.c. of water, is treated with 5 c.c. of nitric acid, heated on the hot plate, and solid ammonium persulphate is added until the mixture is colourless; a yellow coloration, if persistent, can be removed by boiling for a few minutes after the addition of a few c.c. of water and several grams of ammonium persulphate all at once. The volume is made up to 100 c.c., 5 c.c. of saturated sodium ammonium hydrogen phosphate solution are added, followed by an excess of magnesia mixture; any precipitate which forms is dissolved by dilute nitric acid. The solution is heated nearly to the b. p., an excess of aqueous ammonia is added, and, after cooling and keeping for two hours, the precipitate is collected, washed with dilute aqueous ammonia, returned, together with the filter, to the precipitation flask, and dissolved in 70 c.c. of dilute hydrochloric acid (three parts of acid to two parts of water). The solution is cooled, shaken for one minute with 3 grams of potassium iodide dissolved in

6 c.c. of water, 70 c.c. of water are then added, and [redacted] iodine titrated at once with thiosulphate.

CHEMICAL A[redacted]CTS.

Detection of Arsenic in Salvarsan and Neosalvarsan. F. UTZ (*Pharm. Zentr.-h.*, 1920, **61**, 39—42).—The substance is decomposed by heating with a small quantity of sulphuric acid and ammonium persulphate, or with hydrogen peroxide and ferrous sulphate, the solution then diluted, and treated with stannous chloride solution. After a time, the arsenic forms a brown, flocculent precipitate. When a portion of either substance is dissolved in dilute hydrochloric acid in a platinum basin, and a fragment of zinc is added, a brown stain is obtained on the platinum surface. Another test consists in dissolving the substance in concentrated sodium thiosulphate solution and adding hydrochloric acid; sulphur is precipitated, and this is soon coloured bright yellow by the precipitation of arsenic sulphide, which may be separated and identified by the stannous chloride test.

W. P. S.

Renovation of Combustion Tubes. J. DORSMAN (*Chem. Weekblad*, 1920, **17**, 132).—Combustion tubes which have been used for the analysis of substances containing halogens may be renovated as follows. A wash-bottle filled with water is connected to one end of the tube. To the other end an empty U-tube is fitted, connected to a pump. A stream of moist air is drawn through the tube while still red hot. Copper halogen compounds and iodine condense in the cold end and in the U-tube. These may be removed by a piece of wet filter paper. When no further condensation takes place, dry air is drawn through the tube, which is then ready for further use. W. S. M.

Use of Soda-lime in the Calcium Chloride Tube of the Potassium Hydroxide Absorption Apparatus. J. FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 363—364).—Further experiments with gaseous mixtures containing varying proportions of carbon dioxide have confirmed the previous conclusion (this vol., ii, 192) that the use of soda-lime in the calcium chloride tubes of a potassium hydroxide absorption vessel is not only superfluous, but may even be disadvantageous, leading to loss of water. The general belief that potassium hydroxide solution absorbs carbon dioxide less efficiently than soda-lime is probably attributable to the use of absorption apparatus with calcium chloride tubes of insufficient length. The loss of moisture depends on the tension of the absorption agent, the velocity of the gas and the duration of absorption, and is proportional to the last two factors. For the amount of gas evolved in an ordinary elementary analysis, a short calcium chloride tube is sufficient, and no loss of moisture can be observed when the tube is half filled with soda-lime; but in the analysis of carbonates, loss of water is inevitable under such

con[illegible]nd the current of air must be continued for a long time[illegible]ove the whole of the carbon dioxide. Similar conditions occur in the estimation of carbon in iron. The dimensions of a calcium chloride tube suitable for this purpose are: length 4 cm. and diameter 0·8 cm. About 1½ grams of calcium chloride are sufficient to dry the gaseous mixture leaving the potassium hydroxide apparatus, provided that this is charged with potassium hydroxide solution (2:3), that the velocity of the gas does not exceed 0·3 c.c. per second, and that the duration of the absorption does not exceed three hours. C. A. M.

Method for the Preparation of a Hydrochloric Acid Solution of Cuprous Chloride for use in Gas Analysis. F. C. Krauskopf and L. H. Purdy (*J. Ind. Eng. Chem.*, 1920, **12**, 158—161).—A solution of stannous chloride was prepared by heating on a sand-bath, to slow boiling, 300 grams of metallic tin contained in a 500 c.c. flask and covered with concentrated hydrochloric acid, a small amount of fresh acid being added from time to time until the solution was saturated with stannous chloride. The solution was then filtered and stored in a flask containing metallic tin to prevent oxidation. A portion of this solution was mixed with cuprous chloride solution and concentrated hydrochloric acid to obtain a solution of cuprous chloride of approximately the same copper and acid content as a corresponding solution of cuprous chloride, free from other salts, prepared by reducing cupric chloride with copper in acid solution. The two solutions were compared by the absorption, in Hempel double pipettes, in the usual way, of carbon monoxide evolved from oxalic acid by the action of sulphuric acid. Figures were obtained which indicate that the efficiency of cuprous chloride solution for the absorption of carbon monoxide is not deleteriously affected by the presence of relatively large amounts of stannous and stannic chlorides; a satisfactory reagent is obtained by reducing cupric chloride in acid solution by means of stannous chloride, and if a small excess of stannous chloride is used, the solution may be exposed to air during transference from one vessel to another without becoming oxidised. Further, the solution may be renewed, after saturation with carbon monoxide, by heating at 60—70° to drive off the gas, a few drops of concentrated stannous chloride solution being added to correct any oxidation which might occur. S. S. A.

Estimation of Carbon Dioxide, Oxygen, and Combustible Gases by Krogh's Method of Micro-analysis. Hans Oluf Schmit-Jensen (*Biochem. J.*, 1920, **14**, 4—24).—It is shown that Krogh's micro-gas analysis apparatus may be used to estimate hydrogen and carbon monoxide in very small gas samples (*Skand. Arch. Physiol.*, 1908, **20**, 279). As absorbent for hydrogen, a solution of 0·66 gram of colloidal palladium and 0·42 gram of sodium picrate in 20 grams of distilled water is used, and as

absorbent for carbon monoxide an acid solution of cuprous chloride. A modification of Krogh's apparatus is described by means of which it is possible to estimate carbon dioxide and oxygen by absorption, hydrogen and methane by combustion, and carbon monoxide either by absorption or combustion. The hydrogen and methane can only be estimated by combustion if the bubble of gas has a volume of at least 80 cu. mm.; nitrogen is also taken by difference. The fractional combustion of hydrogen and methane is also possible by means of this apparatus. The average error in the readings is about ±0·1 mm. This systematic error is different with the different gases, and in the case of oxygen, hydrogen, methane, and carbon dioxide is of no practical importance, but it must be taken into consideration with carbon dioxide. A small receiver for collecting gas samples is described. J. F. S.

Direct Estimation of Potassium and Sodium in Small Quantities of Blood. B. KRAMER (*J. Biol. Chem.*, 1920, **41**, 263—274).—The method for potassium is a modification of the sodium cobaltinitrite method capable of being used for 1 c.c. of blood or 3—5 c.c. of plasma or serum. The sodium process is based on the precipitation of that element as the pyroantimonate, which is weighed as such. The potassium content of normal human serum varies between 16 and 22 mg. per 100 c.c. of serum. The sodium content has been found in both normal children and adults to vary between 280 and 310 mg. per 100 c.c. of serum. J. C. D.

Estimation of Zinc in Organic Materials, such as Food, Urine, and Excrement. The Zinc Content of Reagents and Analytical Vessels. A. WEITZEL (*Arb. Gesundh. Amt.*, 1919, **51**, 476—493; from *Chem. Zentr.*, 1920, ii, 5—6).—Two methods are described for the estimation of zinc in organic substances. In the first of these, the material is converted into ash, either by the wet or dry process; the latter is dissolved in acid, copper, etc., is removed by hydrogen sulphide, and zinc is precipitated from the acid filtrate by potassium ferrocyanide. The zinc ferrocyanide is decomposed by concentrated sulphuric acid, zinc is precipitated in the usual manner with ammonium sulphide, the precipitate is dissolved in hydrochloric acid, and the zinc is again precipitated by hydrogen sulphide from acetic acid solution. The sulphide is finally dissolved in 1% hydrochloric acid, the zinc is precipitated with sodium carbonate, and weighed as the oxide. The second method is identical with the first as far as the separation of sulphides of copper, etc. Ferrous compounds are then oxidised by nitric acid, sodium hydroxide is added, and the disturbing effect of phosphates is overcome by acidification with acetic acid. The residue left on filtration is separated as completely as possible from the mother liquor and dissolved in dilute hydrochloric acid; it is again treated with sodium hydroxide and acetic acid, and, if necessary, the process is repeated until zinc can no

longer [redacted]tected in the acid filtrate by means of potassium ferrocyanide. The united acetic acid filtrates are saturated with hydrogen sulphide. The details of the two methods are minutely described in the original. Either process permits an exact estimation of zinc as oxide in urine, excrement, animal organs and tissues, and in foods, even if the metal is only present in minimal amounts. It is a matter of indifference whether the organic material is oxidised by the wet or dry process. The second method is to be preferred to the potassium ferrocyanide process, since it requires a smaller number and smaller amounts of reagents, and can be carried out in a shorter time. If the directions are closely followed, and pure reagents free from zinc are used, so little zinc passes into the material under investigation, either from the reagents or from the Jena-glass flasks, which contain considerable quantities of zinc, that it need not be taken into account even for the most accurate analyses. Otherwise, in those cases in which concentrated solutions of alkali hydroxide or phosphoric acid are boiled, or even small quantities of fluorides are warmed with mineral acids in vessels made of glass containing zinc, the possibility of the passage of zinc from the vessel into the material under investigation must always be taken into account; in these circumstances, the use of vessels made of glass free from zinc is advisable. H. W.

Estimation of Mercury in Organic Combination by means of Zinc Filings. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1920, [vii], **21**, 85—91).—A modification of a method described previously (A., 1918, ii, 276) is recommended. The substance is dissolved by heating with alcohol, and the solution is then treated with hydrochloric acid and zinc filings. With mercury benzoate and mercury salicylate, the reduction with zinc is carried out in sodium hydroxide solution containing potassium iodide, and any excess of zinc is dissolved subsequently by treatment with hydrochloric acid. W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. L. BRANDT (*Chem. Zeit.*, 1920, **44**, 101—103, 121—122).—Compare A., 1919, ii, 373, 480).—A further criticism of the method described by Schwarz and Rolfes (A., 1919, ii, 170). W. P. S.

The Analysis of Wulfenite Earths from Mies. E. DITTLER (*Centr. Min.*, 1919, 225—227).—A method has been devised by which calcium, lead, molybdenum, and zinc can be estimated in a single sample of the mineral. About a gram of the finely powdered material is digested successively with hydrochloric and nitric acid until the residue is no longer black. Digestion is then continued with sulphuric acid to convert the calcium and lead into sulphates, and the solution is diluted and filtered, the residue being washed several times with dilute sulphuric acid. The residue is then extracted with ammonium acetate solution, which dissolves both

calcium and lead. These are again precipitated as phosphates, weighed in a Neubauer platinum crucible, then dissolved in hydrochloric acid, the calcium precipitated as oxalate, and the lead estimated by difference. The acid solution containing the molybdenum and zinc is neutralised with ammonia, the iron present precipitated by addition of ammonium chloride and filtered, the solution made strongly ammoniacal, and saturated with hydrogen sulphide. The zinc sulphide is then salted out by addition of ammonium thiocyanate, and the molybdenum determined in the filtrate by known methods. E. H. R.

Separation of Zirconium and Titanium as the Phosphates. JAMES BROWN and H. T. MADDEN (*J. Amer. Chem. Soc.*, 1920, **42**, 36—39).—Zirconium and titanium may be separated and estimated by the following method. The solution, containing 1—2% by volume of sulphuric acid, is treated with an excess of hydrogen peroxide, and then with an excess of disodium or diammonium phosphate, and the solution kept overnight. The precipitated zirconium phosphate is collected and washed with water containing a few drops of sulphuric acid and a little hydrogen peroxide. If, as is usually the case, the precipitate is coloured yellow by titanium, it is fused with sodium carbonate, extracted with water, and redissolved by fusing with potassium hydrogen sulphate, and then treating with dilute sulphuric acid. The zirconium is then reprecipitated as above, and if the precipitate is colourless, all the titanium has been removed. The zirconium phosphate is now converted into oxide by fusing with sodium carbonate, extracting with water, dissolving the residue in hydrochloric acid, and precipitating with ammonia. The precipitate is washed, dried, ignited, and weighed as the dioxide. The combined filtrates from the zirconium precipitation are boiled to decompose hydrogen peroxide, and the acidity adjusted so that the content of sulphuric acid is about 2% by volume. An excess of disodium or diammonium phosphate is added, the mixture kept for one hour, and then filtered. The precipitate of titanium phosphate is washed, converted into the dioxide, as in the case of zirconium, and weighed. The results given in the paper show that the method is capable of a high degree of accuracy. J. F. S.

Testing of Chloroform. F. UTZ (*Pharm. Zentr.-h.*, 1917, **58**, 1—5).—The author has investigated, in particular, the benzidine test for the detection of decomposition products in chloroform. When benzidine is dissolved in pure chloroform, the solution remains unchanged for twenty-four hours if kept in a dark place; if chloral is present, a faint red coloration develops at first, and changes to bluish-red after a time. A turbidity forms immediately if the chloroform contains carbonyl chloride, hydrochloric acid, or chlorine, and a flocculent precipitate may separate. W. P. S.

The Reduction of Aromatic Nitro-compounds by Stannous Chloride and by Titanous Chloride, and their Volumetric Estimation. DANIEL FLORENTIN and HENRI VANDENBERGHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 158—166).—The estimation of nitro-groups by reduction with stannous chloride and titration of the excess of the latter with iodine solution in neutral or acid medium (compare Altmann, A., 1901, ii, 475; Druce, A., 1919, ii, 199), gives satisfactory results with nitrobenzene and various di- and tri-nitro-derivatives, but, contrary to the results obtained by Druce (*loc. cit.*), the authors find that the results obtained for the mononitrotoluenes are too low, owing to the formation of *p*-chlorotoluidines.

Titanous chloride quantitatively reduces the nitro-compounds according to the equation $C_6H_5{\cdot}NO_2 + 6TiCl_3 + 6HCl = C_6H_5{\cdot}NH_2 + 6TiCl_4 + 2H_2O$, except in the case of *o*-nitrotoluene, which gives results which are about 3% too low. The excess of titanous chloride is determined by titrating it into a known volume of standard ferric sulphate solution, using ammonium thiocyanate as an indicator. W. G.

Differentiation of Methyl and Ethyl Alcohols. TH. SABALITSCHKA (*Pharm. Zentr.-h.*, 1920, **61**, 78—79).—Although the copper sulphate test (compare Pannwitz, this vol., ii, 62) has a limited use for the detection of methyl alcohol in ethyl alcohol in the absence of water, it is untrustworthy in the case of dilute alcohols. W. P. S.

The Estimation of Incompletely Nitrated Phenol in the Mother Liquors from Picric Acid by means of Bromine. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 127—138).—The results obtained by Jolibois's method, by the action of bromine on the incompletely nitrated phenol in the mother liquors from picric acid are inaccurate and variable. The results obtained are too high, and vary with the time and temperature of contact of the bromine with the mother liquors and the amount of bromine in excess. It is shown that these mother liquors contain a mixture of sodium 2:4-dinitrophenol-*o*-sulphonate and sodium 2:6-dinitrophenol-*p*-sulphonate in variable proportions, together with some sodium nitrophenolsulphonate. The action of the bromine on each of the dinitrophenolsulphonates varies with the conditions given above; the mononitrophenolsulphonates tend to give dibromo-derivatives, and any picric acid remaining in the mother liquors is acted on by the bromine, all of these changes tending to vitiate the results obtained by Jolibois's method. W. G.

The Estimation of Incompletely Nitrated Phenol in the Mother Liquors from Picric Acid; the Ratio between the Composition of these Mother Liquors and the Yield of a Manufacture of Picric Acid. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 138—140).—Marqueyrol and

Loriette's method is slightly modified. The mother liquors are completely nitrated, and the resulting picric acid is collected and estimated volumetrically by titration with $N/10$-sodium hydroxide. It is necessary to apply a correction for the amount of picric acid dissolved in the water with which the precipitate is washed. [See, further, *J. Soc. Chem. Ind.*, 1920, 248A.]

W. G.

Estimation of Traces of $\beta\beta'$-Dichloroethyl Sulphide [Mustard Gas] in Air. MAX YABLIK, G. ST. J. PERROTT, and N. H. FURMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 266—274).—The method is based on the observation that a solution of selenious acid in sulphuric acid (1:1) is reduced by traces of $\beta\beta'$-dichloroethyl sulphide, giving an orange-red suspension of selenium; the presence of about 0·005 mg. of dichloroethyl sulphide can be detected in this manner. The estimation of the vapour in air is effected by bubbling the mixture through a suitable absorbent, such as a 1% solution of selenium dioxide in water, adding 10 c.c. of a solution of selenious acid in sulphuric acid, care being taken to use the latter in such a manner that a 1:1 solution is finally obtained, and also that the concentration of selenious acid in the ultimate mixture is the same as in the absorbing mixture. The solution is then heated for ten minutes in a bath at 85°, cooled, and the strength estimated by nephelometric comparison with standard solutions prepared from weighed quantities of the reagents. The process is available for amounts of substance between 0·1 mg. and 0·01 mg., with a maximum error of 0·005 mg. The temperature at which the solution is heated in process of "developing" can vary 5° in either direction without affecting the character of the suspension. The method is remarkably free from the necessity for extreme purity of original solution, cleanliness of glassware, etc., which obtains in silver haloid nephelometry. It was not found possible to use good solvents for dichloroethyl sulphide as absorbing media, and then determine the strength of the solutions by the proposed method, since the only suitable solvent (alcohol and acetic acid) reduced the selenious acid to some extent. The selenious reagent is not specific to mustard gas: arsine and the substituted arsines, and several other toxic gases, react with it vigorously.

Attempts to determine the strength of the suspension colorimetrically were not successful. H. W.

The Nephelometric Values of Cholesterol and the Higher Fatty Acids. II. F. A. CSONKA (*J. Biol. Chem.*, 1920, 41, 243—249).—The nephelometric values of oleic acid and cholesterol were found to be influenced by the hydrolysis, as well as by the addition of certain substances which alone, in similar circumstances, do not produce any turbidity. These influencing agents are exemplified by the use of gelatin as a protective colloid.

J. C. D.

Formation of β-Methylumbelliferone as a Reaction of Acetoacetic Acid and its Esters. VICTOR ARREGUINE and EDOUARD D. GARCIA (*Ann. Chim. anal.*, 1920, [ii], **2**, 36—41, *Anal. Soc. Quim. Argentina*, 1919, **7**, 424—432).—In hydrochloric acid solution, acetoacetic acid condenses with resorcinol to form β-methylumbelliferone, and the latter exhibits an intense blue fluorescence when the solution is rendered slightly ammoniacal. To make the test, 2 c.c. of hydrochloric acid containing a trace of acetoacetic acid or ethyl acetoacetate and 0·1 gram of resorcinol are boiled for a few minutes, cooled, diluted with water, and treated with a slight excess of ammonia. In the case of urine, 50 c.c. of the sample are treated with three drops of hydrochloric acid and extracted first with 5 c.c. and then with 3 c.c. of carbon tetrachloride; the latter solution is evaporated to about 3 c.c., and then tested as described. The test will detect 0·00002 gram of acetoacetic acid in 5 c.c. of urine. The reaction is specific, and is not given by acetone or β-hydroxybutyric acid.

W. P. S.

Estimation of Acetone and Acetoacetic Acid with Autenreith's Colorimeter. EMIL LENK (*Münch. med. Woch.*, 1919, **66**, 1119—1120; from *Chem. Zentr.*, 1919, iv, 995).—A reply to Schall (this vol., ii, 63), in which it is pointed out that the latter has simply adopted the author's method with the substitution of Autenreith's colorimeter for a measuring cylinder.

H. W.

Analysis of Acetone by Messinger's Method. LEO FRANK GOODWIN (*J. Amer. Chem. Soc.*, 1920, **42**, 39—45).—Messinger's method for the analysis of acetone (A., 1889, 313) has been critically investigated. The method consists in shaking acetone in the presence of alkali hydroxide with an excess of iodine. After ten minutes, the solution is acidified, and the excess of iodine titrated with a standard solution of sodium thiosulphate. It is shown that under proper conditions the method gives accurate and concordant results. The effect of keeping, the method of shaking and adding the iodine solution, the effect of an excess of acid, and the dilution have all been investigated and found to be without influence on the results. It is shown that methyl and ethyl alcohol if present both use up a certain amount of iodine. J. F. S.

The Acetone Concentration in Blood, Urine, and Alveolar Air. I. A Micro-method for the Estimation of Acetone in Blood, Based on the Iodoform Method. ERIK MATTEO PROCHET WIDMARK (*Biochem. J.*, 1919, **13**, 430—445).—The blood is drawn from the finger or ear lobe into a capillary pipette graduated to 100 c.mm., and is then transferred into the flask of the distillation apparatus, in which there has previously been placed 10 c.c. of 1% phosphoric acid. The pipette is washed out several times with the acid. The distillation must be carried out within two or three hours of the drawing of the blood, and the distillate is collected in a cooled test-tube containing 3 c.c. of

N/2-sodium hydroxide and 2 c.c. of *N*/200- or *N*/100-iodine solution, according to the amount of acetone. The residual iodine is titrated with equivalent sodium thiosulphate after the contents of the tube have been treated with 3·5 c.c. of *N*/2-sulphuric acid. The presence of ethyl alcohol in the blood has no effect on the results of the titration. As a micro-method, the process is not applicable to normal blood and urine, but gives trustworthy results in pathological conditions where there is an increased amount of acetone in these fluids. J. C. D.

Estimation of Acetone Substances. N. O. ENGFELDT (*Acta med. scand.*, 1919, **52**, 311—366; from *Chem. Zentr.*, 1920, ii, 161—162).—Salén's proposed modification (*Nord. med. ark. avd.*, 1918, ii, **51**, No. 11) of the author's previous method for the estimation of acetone substances in urine is unsatisfactory, since errors of 24·5—41·5% occur. Recent investigations lead to a modification of the method, which is now carried out in the following manner. Precipitation of the urine is effected with ammonia, lead acetate, and alum in an exactly specified manner, and, after dilution and acidification with concentrated sulphuric acid, the acetone is distilled and the distillate is titrated with iodine. Chromate and sulphuric acid are added, and the residue is again distilled; the iodine required is a measure of the β-hydroxybutyric acid. Another estimation, in which, first, concentrated sulphuric acid, and then, shortly afterwards, chromate and sulphuric acid are added, permits the measurement of the total acetone substances of the urine as acetoacetic or β-hydroxybutyric acid by one distillation which can be performed in twenty-five minutes. It should be noted that the presence of alcohol in urine, arising from fermentation of dextrose or imbibed by the patient, disturbs the estimation. Toluene, which is more soluble in urine than in distilled water, is, in 2·5% concentration, an active disinfectant, and is recommended as a preservative, since it does not interfere with the estimation.

The author has elaborated a somewhat similar clinical method for the estimation of acetone substances in blood, the details of which will be published shortly. H. W.

Estimation of Dextrose in the Presence of Lactose. E. HILDT (*J. Pharm. Chim.*, 1920, [vii], **21**, 136—137; *Ann. Chim. anal.*, 1920, [ii], **2**, 78—80; *Ann. Falsif.*, 1920, **13**, 21—25). —A Fehling's solution is used, 10 c.c. of which correspond with 0·048 gram of dextrose and 0·071 gram of lactose hydrate or 0·051 gram of lactose after hydrolysis. The solution containing the two sugars is titrated direct into 10 c.c. of the Fehling's solution, and again after hydrolysis. For the hydrolysis, an amount of the sugar solution containing not more than 1 gram of lactose is heated for six hours at 95—98° with 20 c.c. of an 18% solution of sodium benzenesulphonate in *N*-sulphuric acid, after making the mixture up to 100 c.c. with distilled water. W. G.

Estimation of Sugar in Diabetic Blood. G. VIGEVANI (*Boll. Chim. farm.*, 1919, **58**, 436—439).—Two c.c. of the blood are mixed with 100 c.c. of potassium chloride solution (saturated potassium chloride solution 340 c.c., hydrochloric acid 0·375 c.c., and water 160 c.c.), 50 c.c. of the mixture boiled for five minutes, filtered from the precipitated proteins, the filtrate made up to definite volume, and 10 c.c. introduced into an Erlenmeyer flask, round the neck of which rubber tubing has been fixed. From 1 to 2 c.c. (according to the amount of dextrose) of a copper solution (copper sulphate 2·2, potassium hydrogen carbonate 80, potassium carbonate 50, potassium chloride 53 grams; water, 500 c.c.) are added, the mixture boiled for three minutes, and the rubber tube closed with a clip, so that a vacuum is produced within the flask after cooling. A current of carbon dioxide is then introduced, and the liquid titrated with iodine solution ($N/10$-hydrochloric acid 5 c.c., iodine 0·0635 gram, potassium iodide 2 grams, 2% potassium iodate solution 2 c.c., and water to 100 c.c.), with starch solution (2 grams of soluble starch in 100 grams of saturated potassium chloride solution) as indicator. The copper reduced by the dextrose reacts with the iodine solution. The latter is previously standardised on pure dextrose which has been dried at 100°. C. A. M.

Method of Identification of Amino-acids. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 743—754).—The principle of the method, which in this paper deals only with phenylalanine, consists in converting the amino-acid into the hydroxy-acid and determining the m. p. of the latter.

A solution of 0·2—0·3 gram of phenylalanine in a slight excess of acid (preferably sulphuric acid) is treated at 80° with a solution of sodium nitrite very slowly until nitrogen ceases to be evolved. The solution is boiled for two to three minutes, diluted with water to twice or thrice its volume, boiled with calcium carbonate for twenty to thirty minutes, filtered, and concentrated to 5—7 c.c. Calcium phenyl-lactate is precipitated by the addition of a few drops of $2M$-calcium chloride. The phenyl-lactate is dissolved in 2 c.c. of concentrated hydrochloric acid, and the m. p. of the phenyl-lactic acid which separates after several hours is determined after recrystallisation from alcohol or benzene.

The author has isolated another hydroxy-acid, m. p. 93—94°, mol. wt. 176, which is very strongly lævorotatory, and is probably derived from an isomeride of phenylalanine.

The phenylacetaldehyde obtained by heating 0·01 gram of phenyl-lactic acid develops with 2—3 c.c. of 50% alcoholic sulphuric acid a permanent, green coloration after keeping for several hours.

CHEMICAL ABSTRACTS.

Detection of Carbamide. J. F. A. POOL (*Pharm. Weekblad*, 1920, **57**, 178—179).—The presence of the enzyme urease may be detected in soja beans by means of the colour effects produced in a jelly containing 2% of carbamide and aqueous yeast extract (A.,

1916, i, 536). Conversely, the presence of carbamide in solutions may be shown by making the liquid neutral to phenolphthaleïn, adding 2% of agar-agar, boiling, and placing a small section of soja bean on a portion of the jelly solidified in a watch-glass. After some time a red coloration begins to spread from the bean outwards. W. S. M.

Method of Estimating Quinine and Strychnine when Occurring in Common Solution. A. R. BLISS (*J. Amer. Pharm. Assoc.*, 1919, **8**, 804—807).—The method is based on the solubility of strychnine in water (1 in 6420) and its slight solubility in ethyl ether. Fifty c.c. of the preparation are freed from alcohol, a slight excess of citric acid is added, followed by an excess of aqueous ammonia, the total alkaloids are extracted by chloroform-ether mixture, the extract is evaporated, and the residue is dried and weighed. The total alkaloids are dissolved in dilute sulphuric acid, an excess of water (more than 6500 times the weight of the strychnine) is added, together with an excess of aqueous ammonia, and the mixture is shaken seven times with ether. The ethereal extracts are united, washed with 5 c.c. of water and evaporated, and the residue is dried and weighed as quinine. The residual aqueous solution is extracted seven times with chloroform, the extracts are united and evaporated, and the residue is dried and weighed as strychnine. Excellent results are recorded for solutions of approximately known strength. CHEMICAL ABSTRACTS.

A Modification of the Francis-Connell Method of Estimating Hydrocyanic Acid. PAUL MENAUL and C. T. DOWELL (*J. Agric. Res.*, 1920, **18**, 447—450).—See this vol., i, 359.

The Toxicological Detection of Physostigmine [Eserine]. H. FÜHNER (*Biochem. Zeitsch.*, 1918, **92**, 347—355).—Quantities of 5/1000—1/100 mg. of eserine can be detected by means of the biological eye reaction in the cat. The author finds that in the case of the plain muscle of the leech, minute quantities of eserine in the presence of acetylcholine increase the contraction of the muscle brought about only to a small extent by acetylcholine alone. By this joint action of the two drugs on the muscle of the leech, 1/10,000 mg. of eserine can be detected with certainty. S. S. Z.

A Quantitative Biological Method for the Estimation of Nicotine. H. FÜHNER (*Biochem. Zeitsch.*, 1918, **92**, 355—364). —By means of the contraction produced by the action of nicotine on the plain muscle of the leech, it is possible to estimate quantitatively 1/100 mg. of the drug. The myograph of the nicotine solution of unknown strength is compared with that of a solution of known strength. S. S. Z.

LI.—*The Falling Sphere Viscosimeter.*

By William Howieson Gibson and Laura Mary Jacobs.

Although the rate of fall of a steel ball through a viscous liquid is frequently made use of as an empirical test, little work has been done on the application of this method to the determination of the absolute viscosity of liquids.

In view of the simplicity of the method and the advantages it possesses when very viscous liquids are being examined, it was felt that a standardised falling sphere viscosimeter would be of value in certain researches on nitrocellulose solutions.

The conditions, corrections, and sources of error in applying this method were therefore considered, and an apparatus was specified capable of measuring the absolute viscosity of a wide range of liquids with considerable accuracy. In this connexion, we are indebted to Mr. W. MacNab for a sketch of the apparatus which he had found convenient for the comparison of nitrocellulose solutions.

The apparatus has now been in use in Government laboratories for testing purposes since February, 1917, with satisfactory results, so the initial work is now published, in the belief that it may have further applications.

The velocity of a sphere falling vertically in a fluid in relation to viscosity was investigated mathematically by Stokes (see Lamb, "Hydrodynamics," p. 587 *et seq.*), who derived the well-known equation

$$V = \frac{2}{9} g r^2 \frac{s - \sigma}{\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V is the velocity of the sphere, r the radius and s the density of the sphere, and σ the density and η the viscosity of the liquid.

This equation holds only when the conditions are such that $\frac{Vr(s-\sigma)}{\eta}$ is small, since from dimensional considerations it is apparent that the general expression for the resistance experienced by a sphere in falling through a liquid is

$$\left[\frac{Vr(s-\sigma)}{\eta}\right]^n \frac{\eta^2}{s-\sigma},$$

and this only simplifies to $Vr\eta$, as required by Stokes's equation, when $n=1$. Higher powers of n can only be neglected if

$\frac{Vr(s-\sigma)}{\eta}$ is small (see Edser, "General Physics," p. 489, or Poynting and Thomson, "Properties of Matter," p. 222).

Stokes's equation applies only to a sphere falling through an infinite extent of liquid, but the velocity of a small sphere falling axially through a viscous liquid in a cylinder has been discussed mathematically by Ladenburg (*Ann. Physik*, 1907, [iv], **23**, 9, 447), Lord Rayleigh (*Phil. Mag.*, 1893, [v], **36**, 354), and Allen (*ibid.*, 1900, [v], **50**, 323), and Ladenburg (*Ann. Physik*, 1907, [iv], **22**, 287) made use of the principle for the determination of the viscosity of Venice turpentine under pressure. Sheppard (*J. Ind. Eng. Chem.*, 1917, **9**, 523) has used the method of the falling sphere for the determination of the absolute viscosity of viscous liquids, such as solutions of nitrocellulose, but the correction formula for the effect of the walls of the vessel on the time of fall of the ball applied by him is not that reached mathematically by Ladenburg, Rayleigh, and Allen, which we have found to be correct experimentally. Further, the comparatively large-sized balls used by Sheppard are not an advantage.

According to Ladenburg, there are two linear corrections to be applied to the simple Stokes' equation for the case of a small sphere falling axially through a viscous liquid in a cylindrical tube, a correction for wall-effect and one for end-effect.

The correction for wall-effect is

$$V(1+2{\cdot}4\,x) = V_{\infty} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x is the ratio of the radius of the sphere to that of the cylinder, V is the velocity of the sphere, and V_{∞} the velocity of the sphere corrected for an infinite medium. This formula was confirmed experimentally for tubes and balls of the radii used by us, but fails when x becomes large, hence for a steel ball of given diameter the diameter of the tube employed must be sufficiently large for the correction to apply. Sheppard used for a correction the empirical formula $T = T_{\infty} + \frac{c}{(r-1)^n}$, where T is the time of fall of the sphere through a length s, T_{∞} the time of fall in an infinite medium, r the ratio of the radius of the cylinder to that of the sphere, c a constant depending on the diameter of the sphere, and n is a constant taken by Sheppard as 2.

From the form of this expression, it is an endeavour to apply a correction for cases when the diameter of the tube is not large enough relatively to the sphere for the linear correction of Ladenburg to apply, but although the expression may fit the author's

data when suitable constants are chosen, this does not prove that the value of T_∞ obtained is the correct one.

The correction for end-effect has not been taken into consideration by Sheppard. It is of less importance than that for wall-effect, but is appreciable. If the velocity is measured in the middle third of the tube, the correction is

$$V_\infty = \left(1 + 3{\cdot}3\,\frac{r}{h}\right)V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where r is the radius of the sphere and h is the height of the liquid.

The complete equation, including both corrections, for the falling sphere viscosimeter is consequently

$$9\eta V(1 + 2{\cdot}4\,x)\left(1 + 3{\cdot}3\,\frac{r}{h}\right) = 2gr^2(s - \sigma) \quad . \quad . \quad . \quad (4)$$

or, if the time of fall T through a length s is measured,

$$9\eta s(1 + 2{\cdot}4\,x)\left(1 + 3{\cdot}3\,\frac{r}{h}\right) = 2\,gr^2(s - \sigma)T \,. \quad . \quad . \quad . \quad (5)$$

If spheres of equal radius are used in tubes of the same dimensions, the only variables are relative density, viscosity of the liquid, and time of fall. A simple equation,

$$\frac{\eta}{\eta_1} = \frac{(s - \sigma)T}{(s - \sigma_1)T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

resembling the expression used for the Ostwald pattern of capillary viscosimeter, can then be employed to obtain the viscosity of a liquid when the time of fall for another liquid of known viscosity is known. This permits of the standardisation of viscosimeter tubes by means of a standard liquid the viscosity of which has been determined, either in a tube, the dimensions of which have been accurately measured, or by another method.

Selection of Components.

The considerations which influenced the specification of the apparatus may now be discussed.

In the choice of a sphere, uniformity of diameter is most important, and steel ball-bearings are very satisfactory in this respect. They are guaranteed by the makers to be correct within 0·0025 mm. Tested by the measurement of one gross of balls, this was found to be the case. The possible error on the radius of the sphere when a ball of 0·15 cm. in diameter is taken is therefore only 0·16 per cent.

A ball of 0·15 cm. in diameter was chosen as the standard size, as it was the smallest stock size. The advantages of using the smallest ball available are that the correction factors may be applied to tubes of small diameter, and since the expression $\frac{Vr(s-\sigma)}{\eta}$, which must be small for Stokes's equation to hold, decreases with r, that valid results may be obtained over a wider range of liquids. The density of the steel of which the ball-bearings are composed was determined for one gross of balls, and found to be 7·65.

It is unlikely that great variations exist in the density of ball-bearings, and error can always be avoided by determining the density of the balls in use.

Before the standard diameter for the viscosimeter tube was fixed, many experiments were made in which a sample of castor oil was used as the liquid, and the times of fall of standard 0·15 cm. spheres in tubes of different diameters were determined.

The results obtained at 20° with five tubes are given in table I.

TABLE I.

Diameter of tube. Cm.	Time of fall for 15 cm. Seconds.	x.	Time of fall, infinite medium. Seconds.
0·85	25·2	0·187	17·4
1·14	21·8	0·1395	16·3
2·10	18·8	0·0757	15·9
3·50	17·7	0·0454	15·95
4·54	17·4	0·0350	16·0

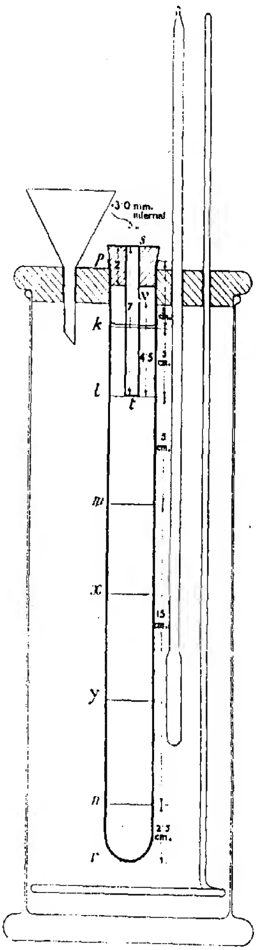
It will be seen that the time of fall, calculated for an infinite medium, becomes constant for the wider tubes. The small differences are ascribed to irregularities in the bore of the tubes.

For the standard tube, an internal diameter of $2 \pm 0{\cdot}05$ cm. was specified as coming within the limit of applicability of the correction factor, whilst being more convenient than wider tubes. The maximum error involved in taking these tubes as exactly 2 cm. in diameter without measurement is 0·4 per cent., since the correction factor for 1·95 cm. is 1·195, for 2 cm. 1·1905, and for 2·05 cm. 1·186. In technical work, an error of this magnitude may often be neglected, but it is preferable to standardise each tube by measuring the time of fall with a liquid of known viscosity for accurate work. If the values of η_1, σ_1, and T_1 for the liquid of known viscosity and s the density of the steel are substituted in equation (6), it becomes

$$\eta = K(s-\sigma)T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where K is a numerical constant involving all the corrections for the particular tube, termed the tube constant.

The total length of the viscosimeter tube was fixed at 29 cm., and it was divided into three 5-cm. lengths for measurement of time of fall, another 5 cm. was allowed for the ball to acquire its uniform velocity, and a further graduation mark fixed the height of the liquid in the tube. To deliver the sphere into the centre of the tube, the following simple device was found satisfactory. The tube was closed by an india-rubber stopper, bored centrally, with a glass tube of 3 mm. internal diameter and 7 cm. long passing through it.



This tube was adjusted to dip 3 cm. below the surface of the liquid in the viscosimeter tube, a small hole in the side wall of the releasing tube just below the stopper serving to adjust the pressure inside and outside the tube. The sphere, when dropped into the releasing tube, travels very slowly down it, and is freed from air bubbles; it then leaves the end below the surface of the liquid with the minimum of disturbance and in the centre of the tube.

The accompanying diagram shows the arrangement of the apparatus.

Viscosity of Castor Oil.—Castor oil was chosen as a convenient standard liquid.

The viscosity of castor oil has been determined over a range of temperature by Kahlbaum and Raber (*Kais. Leop-Carol. Deut. Akad. Naturf. Halle*, 1905, **84**, 203).

Table II gives a few of their results.

TABLE II.

Temperature.	16·1°	19·6°	22·6°	24·8°	26·4°
Viscosity in C.G.S. units	13·704	10·272	7·908	6·592	6·003

The viscosity at 20° is therefore 9·9.

The time of fall of a standard ball through 15 cm. of castor oil in a standard viscosimeter tube of 1 cm. radius at 20° was found to be 19·4 seconds.

Substituting in equation (5), this gave

$$9 \times \eta \times 15 \times 1{\cdot}1905 \times 1{\cdot}0103 = 2 \times 981 \times 0{\cdot}0794^2 \times 6{\cdot}69\,;$$

hence $\eta = 9{\cdot}888$.

The density of the castor oil was 0·96 and the density of the steel 7·65.

The result obtained with the falling sphere viscosimeter is remarkably close to that obtained by Kahlbaum and Raber, and indicates that the instrument may be used with confidence to determine the viscosity of liquids with similar or greater viscosity.

Summary.

The theory of the falling sphere viscosimeter is briefly discussed and the magnitude of some corrections and errors are indicated.

The bearing of these on the design of an instrument for general use is discussed.

The viscosity of castor oil determined by this instrument is shown to agree with the value found by Kahlbaum and Raber.

This work was carried out at the Research Department, Royal Arsenal, Woolwich, and is published by permission of the Director of Artillery, War Office, to whom our thanks are due.

We also desire to express our thanks to Lieut.-Colonel R. A. Craig, C.M.G., and to Sir Robert Robertson, K.B.E., F.R.S., for the interest they have taken in this work.

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LII.—*The Viscosity of Solutions of Cellulose.*

By William Howieson Gibson.

Part I.

During the progress of work in connexion with the manufacture of propellant powders, some observations of general interest on the viscosity of solutions of cellulose have been made, and this paper gives a brief account of this portion of the work.

Very many determinations of viscosity have been made, so a selection only has been given.

A number of determinations of the viscosity of cuprammonium solutions of various forms of cellulose, such as cotton, wood-pulp, etc., were made by Ost (*Zeitsch. angew. Chem.*, 1911, **24**, 1892), who claimed that viscosity determinations carried out by his method gave useful information on the nature and technical value of celluloses.

As the determination of viscosity seemed to be a promising method of obtaining information of technical value, a considerable number of experiments were carried out by Ost's method, but the results were far from satisfactory, owing to the progressive changes which took place in the solution, which are referred to in Ost's paper.

In order to improve the method, elimination of the progressive change in the solutions was essential, and as air-oxidation seemed a probable cause, complete exclusion of air was tried.

The difficulties in obtaining trustworthy viscosity determinations were overcome in this way by the use of the hydrogen capillary viscosimeter, and, later, the falling sphere viscosimeter (see Part II).

Although the hydrogen capillary viscosimeter was somewhat troublesome to manipulate and could only be used for solutions of cellulose up to 1 per cent., it was found very useful in studying the effect of various treatments on cellulose.

The viscosity in C.G.S. units of 1 per cent. solutions in cuprammonium of twenty-eight samples of purified cotton-waste examined in the hydrogen capillary viscosimeter ranged from 4·53 to 0·14, and the viscosity of a trade sample of unpurified waste was found to be 7 units. These results indicated that considerable difference existed between different samples of purified cotton-waste, which could probably be ascribed to difference in treat-

ment. The high viscosity of unpurified cotton was also definitely established.

The effect of variation in the conditions of treatment of cellulose with sodium hydroxide solutions on the viscosity of the product was studied on the laboratory scale, using the hydrogen capillary viscosimeter.

The results obtained in these experiments are given in the following tables, and are plotted in Fig. 1.

TABLE I.

Conditions of boiling. Cotton 100 parts. NaOH 18 parts.	Number of curve in Fig. I.	Viscosity in 1 per cent. solution C.G.S. units. Time of boiling in hours.					
		0.	1½.	3.	6.	9.	12.
Pressure, 5·6 kilos. per sq. cm.							
4 per cent. NaOH solution.	I.	14·48	0·40	0·13	0·09		
2 ,, ,, ,,	II.	14·48	0·54	0·21	0·14		
Pressure, 2·8 kilos. per sq. cm.							
4 per cent. NaOH solution.	III.	14·48	2·51	1·46	0·84	0·45	0·42
2 ,, ,, ,,	IV.	14·48	3·61	2·40	1·87	0·75	0·53
Pressure, 1·4 kilos. per sq. cm.							
4 per cent. NaOH solution.	V.	14·48				2·65	
2 ,, ,, ,,	VI.	14·48				3·90	

TABLE II.

	Parts of NaOH solution to 1 part of cotton.			
	2.	4.	8.	16.
Pressure, 5·6 kilos. per sq. cm.				
Time 1½ hours.				
4 per cent. NaOH solution	0·43	0·40	0·29	0·32
2 ,, ,, ,, ...	1·27	0·72	0·54	0·53

Consideration of these results leads to the following conclusions:

(1) Temperature is the main factor in reducing the viscosity of cotton during boiling with sodium hydroxide.

(2) The viscosity falls rapidly at the beginning of the experiment, and the rate of fall slackens as the boiling continues.

(3) The concentration of sodium hydroxide solution influences the viscosity. With a 2 per cent. solution, the viscosity is

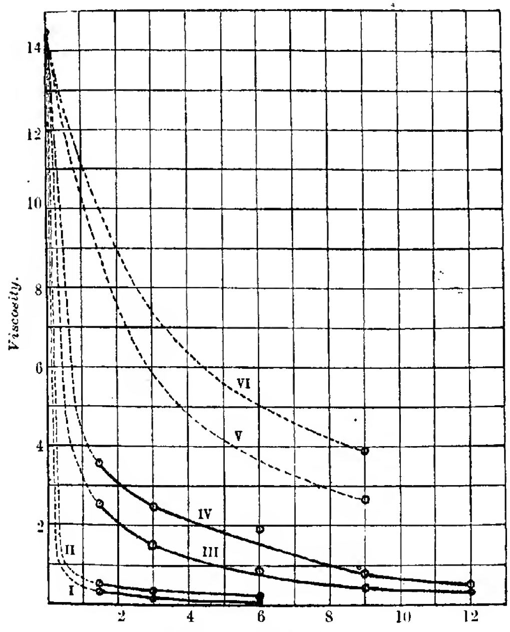
approximately about 50 per cent. higher than with a 4 per cent. solution.

(4) At high temperatures, the viscosity falls so rapidly that the concentration of the solution is of little practical importance.

(5) With mild treatments, the actual difference between concentrated and dilute solutions is more pronounced.

(6) When the proportion of solution to cotton is increased, the

FIG. 1.



viscosity is reduced. This may be due to the concentration of the solution remaining more uniform during the boiling.

The experiments indicated quite clearly that the viscosity of purified cotton could be controlled by controlling the conditions of the boiling process. Examination of samples of bleached and unbleached cotton-waste were made, and led to the conclusion that the process of bleaching with weak bleaching powder solution

had little effect on viscosity. The effect of treating the cotton with sulphuric acid (0·25 per cent.) was found to be negligible; thus, the viscosity of the same sample of cotton before treatment was 0·42 unit, and afterwards 0·45 unit.

Many samples of cotton boiled on the manufacturing scale under various conditions have now been examined with the falling sphere viscosimeter, and several interesting relationships have been indicated. The large-scale work has proved conclusively that the conditions of the boiling process determine the viscosity of the purified cellulose, and it has been found possible by standardising these conditions to keep the viscosity of cotton-waste used for nitration within much narrower limits than heretofore. The results of the determination of the viscosity of one blend of cotton-waste, using different treatments, are given in table III.

TABLE III.

Solution.	Pressure of steam. Kilos. per sq. cm.	Time. Hours.	Viscosity of 2 per cent. solution.
2 per cent. NaOH 2 per cent. Na_2CO_3	Atmospheric.	10	317
2 per cent. NaOH 2 per cent. Na_2CO_3	,,	20	256
4 per cent. NaOH	,,	10	332
4 per cent. NaOH	,,	20	193
2 per cent. NaOH	1·4	10	240
2 per cent. NaOH	,,	20	94
1 per cent. NaOH 3 per cent. Na_2CO_3	2·8	10	172
2 per cent. NaOH 2 per cent. Na_2CO_3	,,	10	129
2 per cent. NaOH 2 per cent. Na_2CO_3	,,	20	19
2 per cent. NaOH	,,	10	73
2 per cent. NaOH	,,	20	24
4 per cent. NaOH	,,	10	48
4 per cent. NaOH	,,	20	4

These results again indicate the importance of temperature in reducing viscosity, and the influence of strength of solution is shown. It is also evident that sodium carbonate is ineffective compared with sodium hydroxide.

The experiments on different classes of waste given in table IV are of considerable interest. In these experiments, the conditions were the same in all cases, but the Eastern cottons give products the viscosity of which is about half that of American cotton of similar grade.

There is also a marked difference in the viscosity obtained with long-fibred cop-waste and short-fibred fly. It is hoped that further work in this direction will enable more definite correlations to be

made between climatic conditions of growth of cotton and the viscosity of solutions, and also between maturity of fibre and viscosity.

TABLE IV.

Treatment.—Ten hours under a pressure of 2·8 kilos. per sq. cm. with 4 parts of 3 per cent. sodium hydroxide solution to 1 part of cotton.

Material.	Viscosity of 2 per cent. solution.
American Fly	128
Eastern Fly	53
American Cops	57
Eastern Cops	26

A further relationship has been shown to exist between the viscosity of cellulose solutions and the viscosity of nitrocellulose solutions. The property inherent in cellulose to which viscosity is due is transmitted to the nitrated derivative. Table V indicates that high viscosity in the cellulose is accompanied by high viscosity in its derivative.

TABLE V.

Viscosity of cotton: 2 per cent. cuprammonium solution.	Viscosity of nitro-cotton: 5 per cent. solution in a mixture of ether and alcohol.
317	67
172	43
48	29
4	10

At the instance of Mr. F. R. Jackson, Director of the Flax Experimental Station at Selby, five samples of flax supplied by him were examined for viscosity by the falling sphere method. The results obtained are given in table VI.

TABLE VI.

	*Viscosity of 1 per cent. solution.
A. Pond retted, hand scutched flax	22·3
B. As *A*, but twice scutched by machine	19·7
C. Twice retted in tanks under controlled conditions	30·2
D. Russian dew-retted, low grade	11·3
E. Originally scutched without retting, fibre then retted and re-scutched	26·5

These preliminary results indicate that the viscosity bears a relationship to the character of the flax; thus, Russian dew-retted, low-grade flax differs widely in viscosity from sample *C*, Selby flax, retted in warm water, and of far superior quality.

The viscosity–concentration curve for cellulose in cuprammonium has been studied, but Arrhenius's simple formula appears only to apply over short ranges of concentration.

A relationship between viscosity and solubility of cellulose in cuprammonium solution is indicated by observations made with a variety of cellulose.

The work has scarcely progressed far enough for wide generalisations to be made, but it seems clear that certain treatments can be applied to cellulose which alter its physical properties profoundly, but produce no decided change in chemical properties. This lends support to the view that the production of cellulose in the plant is a process of polymerisation, the older layers, presumably, being more highly polymerised than new growth; the process of boiling with sodium hydroxide may effect the reverse change and depolymerise the cellulose.

Part II.

[With Leo Spencer and Robert McCall.]

The Hydrogen Capillary Viscosimeter.

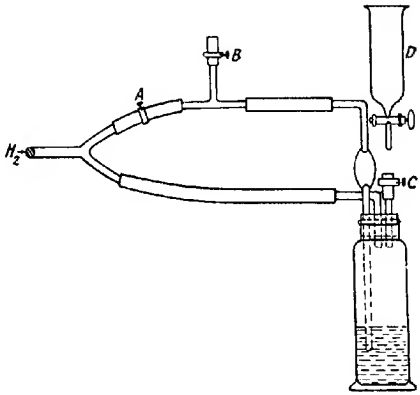
The chief difficulty with Ost's method of determination of viscosity is the progressive alteration which the solutions of cellulose undergo, changes in viscosity occurring all through the process of solution and up to the time of making the determination. Investigation showed that this change was caused by the presence of air and light, so a viscosimeter was devised in which solution of the cellulose was effected in an atmosphere of hydrogen and the influence of light was avoided. With this apparatus, concordant results were obtained, and it was possible to repeat determinations of viscosity of cellulose with satisfactory results. The apparatus consisted of: (1) a Kipp's hydrogen apparatus; (2) a washing bottle filled with sodium hydroxide solution to free the hydrogen from acid; (3) a glass cylinder of about 100 c.c. capacity to contain the cotton and cuprammonium solution, and a three-holed rubber stopper to fit; (4) a capillary viscosimeter, bulb 3—4 c.c., capillary of internal diameter 0·7 mm., length 12—15 cm.; (5) a tap funnel of 10 c.c. capacity to introduce the solution into the containing cylinders; (6) a supply of large glass beads.

The arrangement of the apparatus is shown in Fig. 2.

Procedure.—Half a gram of dry cotton is cut into small pieces to facilitate solution. The cotton, together with six or eight glass

beads, is introduced into the cylinder. The rubber cork containing the viscosimeter and inlet tubes is then inserted, and the air is displaced by a current of hydrogen whilst the cylinder is in an inverted position. A period of less than twenty minutes is necessary for complete displacement of air, and this is most essential, as even minute traces of air lower the viscosity of the cuprammonium solution of cotton. When the displacement of air is complete, 50 c.c. of cuprammonium solution are added in the following manner. The tap funnel, *D*, is attached to the capillary outlet tube at *C*, and the tap is opened for a few seconds to displace any air in the outlet tube and the connexion. The current of hydrogen is then stopped, the clip at *B* unscrewed, and

FIG. 2.



the solution is allowed to run from *D* into the cylinder. The clips at *B* and *C* are then screwed up tightly, the hydrogen is again turned on, and the contents of the cylinder are shaken vigorously until solution is complete. To carry out the determination, the solution is forced up into the viscosimeter bulb by closing the clip at *A* and applying suction at *B*. The clip at *B* is then closed and that at *A* opened, allowing the solution to fall in the capillary tube. The time of fall between two marks is then measured by a stop-watch. The measurement is repeated, with intervening shaking, until the results are seen to be constant, as it is sometimes difficult to tell by inspection whether solution has been complete. Brown paper covers for the cylinder and viscosimeter serve to protect the solution from the action of light. The

viscosimeter is standardised by means of a mixture of glycerol and water; the viscosity of this mixture is then compared with that of water in a viscosimeter of the Ostwald type of smaller bore.

Effect of Air on the Viscosity of Cellulose Solutions.

The following experiment indicates the effect of air on the viscosity of cuprammonium solutions of cellulose. A solution of cotton in cuprammonium was made in the presence of hydrogen, and the hydrogen was then displaced by air.

In one case the solution was allowed to remain without shaking, and in the second the solution was shaken continuously.

Time of contact with air in hours.	Viscosity : Water = 1	
	Standing only.	With shaking.
0	73	60
½	73	8
1	72	4
2	63	3
4	48	2·5
10	31	—
30	16	—
40	12	—

Effect of Light on Viscosity.

In this experiment, a solution of cotton in cuprammonium was made in the presence of hydrogen, and the viscosity was measured. The solution was then exposed to light. The following determinations were made at intervals:

Initial viscosity.	1376.	Water = 1.
After exposure to bright sunlight for 10 minutes	191	
After a further 4½ hours protected from light	186	
After further exposure for 10 minutes	84	
,, ,, ,, 15 ,,	56	
,, ,, ,, 30 ,,	38	
,, ,, ,, 75 ,,	27	

Use of the Falling Sphere Viscosimeter for Cuprammonium Solutions.

It appeared from the work with the hydrogen capillary viscosimeter that the falling sphere viscosimeter (see preceding paper) could be adapted for use with cuprammonium solutions of cellulose. It was necessary to use a narrower tube. 1 cm. in diameter. owing to the deep blue colour of the solution, otherwise the standard apparatus previously described was used.

As more viscous solutions could be dealt with advantageously, 2 per cent. solutions of cellulose in cuprammonium were used.

It was necessary to avoid contact with air during the solution of the cellulose. This is effected by placing 100 c.c. of cuprammonium solution with eight or nine glass beads in a stout, brown glass bottle of 150 c.c. capacity, and adding the weighed quantity of cotton. The bottle is then closed at once with an indiarubber stopper, through which a short capillary tube passes, one end being flush with the bottom of the stopper, the other end being connected by a short length of indiarubber tubing provided with a screw clip, to a second and similar bottle. The latter is closed with a rubber stopper through which pass two short glass tubes, one provided with a glass tap connecting it to the first bottle, the other connecting it by means of a short piece of pressure-tubing provided with a screw clip to the water-pump.

The connexion between the first and second bottle is closed by means of the tap, and the second bottle is exhausted by the pump; the screw clip between the second bottle and the pump is then closed and the glass tap is suddenly opened, when the rapid suction of air from the first bottle into the second causes bubbles to rise from the cuprammonium solution and to displace the air. This operation is repeated three times. The use of the second bottle ensures efficient and standard exhaustion of air without undue loss of ammonia. The screw clip attached to the first bottle, hitherto open, is now closed as tightly as possible, the bottle is detached, and immediately shaken vigorously for five minutes. The bottle is then immersed in a covered bath of water at 20° for eighteen to twenty-four hours with occasional shaking. The viscosimeter tube is filled from the bottle without access of air in the following manner. When solution is complete, the stopper is removed from the bottle without disturbing the liquid, and is replaced by a rubber stopper carrying a short inlet tube reaching to 1 cm. from the bottom of the bottle, and an outlet tube, diameter 5 mm., flush with the bottom of the stopper and about 50 cm. long, the inner end of which is capped by a cover of fine-meshed copper gauze. The viscosimeter tube, exactly 1 cm. diameter, is slipped over the long outlet tube, and the bottle is then inverted without shaking the liquid. The solution flows down into the viscosimeter tube, and, as the latter fills, the outlet tube is raised, but not above the surface of the liquid, care being taken to avoid air bubbles. With highly viscous solutions the flow is accelerated by the application of compressed air to the inlet tube of the bottle. When the tube is filled to within 3 cm. of the top the bottle is removed. The filled viscosimeter tube is then fitted

with a rubber stopper carrying a releasing tube for the steel balls, which should be exactly central. The viscosimeter tube is then placed in a vertical position in the water-bath at 20°, and the determination made by measuring the time of fall of a 0·15 cm. steel ball through 15 cm. With this method of filling, the measurement is made through solution which has not been exposed to air.

Calculation of Absolute Viscosity.

If the mean time of fall of the ball through 15 cm. is t, the absolute viscosity, η, is given by

$$\eta = 0{\cdot}42t,$$

the constant 0·42 including the correction factors. These are determined by calibration with castor oil of known viscosity, thus: Density of cellulose solution, 0·95; viscosity of standard sample of castor oil, 9·888, D 0·96; time of fall of ball through 15 cm. in 1-cm. tube, 23·4 sec.

$$\text{Constant} = \frac{\eta}{t} = \frac{\eta_1(s-\sigma)}{t_1(s-\sigma_1)} = \frac{9{\cdot}888 \times 6{\cdot}7}{23{\cdot}4 \times 6{\cdot}69} = 0{\cdot}423.$$

Study of the Cuprammonium Solution for Cellulose.

Although the main difficulties in the way of trustworthy determinations of the viscosity of solutions of cellulose in cuprammonium disappeared when the precautions used to avoid the action of light and air had been adopted, minor irregularities were still sometimes obtained, and as Ost's method for the preparation of the cuprammonium solution was being followed, this was eventually suspected as the cause of trouble. It was noticed that whilst duplicate experiments carried out on the same day gave results which were quite concordant, irregular results were obtained when an interval of some weeks was allowed to elapse before the duplicate experiment was carried out. A few extreme results may be given to indicate the nature of the discrepancies.

Cotton *A*.	Viscosity in Ost's solution	2·22
	Viscosity 3 weeks later..............	1·50
	Viscosity 6 weeks later..............	1·72
Cotton *B*.	Viscosity in Ost's solution	1·23
	Viscosity 6 weeks later..............	1·50

The analysis of various solutions showed that the variations in copper content were somewhat larger than would be expected from the examples given by Ost.

The extreme figures were:

Copper, grams per litre.	Ammonia, grams per litre.
15·1	196·4
11·6	225·2

When the copper and ammonia contents were intentionally varied widely, it was found that the viscosity of a sample of cotton was affected as follows:

Composition of solution, grams per litre.		Viscosity of cotton.
Cu.	NH_3.	
8·47	266·9	1·64
15·33	202·9	2·52
22·84	175·1	3·54
28·40	129·7	5·44

In the preparation of Ost's solution, besides the apple-green basic copper sulphate, two distinct precipitates are obtained, one pale blue and the other dark blue. Addition of water to the solutions containing these precipitates caused the dark blue needles gradually to dissolve, but left the pale blue precipitate undissolved.

The solutions were found to contain sulphate in quantities which increased as the concentration of the ammonia decreased. The dark blue needles, described by Ost as cuprammonium hydroxide, had the same crystalline form as tetrammine copper sulphate (Found: Cu = 25·84; SO_4 = 37·7. Calc.: Cu = 25·86; SO_4 = 39·1 per cent.). The pale blue precipitate was free from sulphate and was apparently copper hydroxide.

The precipitate of basic copper sulphate used by Ost to prepare his solution therefore appears to dissolve in ammonia as cuprammonium hydroxide and as tetrammine copper sulphate, any excess being left as tetrammine copper sulphate crystals and copper hydroxide.

To obtain further information, the solubilities of tetrammine copper sulphate in ammonia and copper hydroxide in ammonia were determined, with the following results.

Solubility of Tetrammine Copper Sulphate at 15° in Ammonia.

Cu, grams per litre.	NH_3, grams per litre.
0·43	234·1
1·13	222·1
2·37	192·9
3·46	175·8
5·16	153·7
7·66	145·3
11·11	134·0

The solubility of copper hydroxide in ammonia has been previously determined by Bonsdorff (*Zeitsch. anorg. Chem.*, 1904, **41**, 132) and Dawson (T., 1909, **95**, 370). In our work, the copper hydroxide was prepared by triturating basic copper sulphate with sodium hydroxide, as described by Dawson.

Solubility of Copper Hydroxide in Ammonia.

Solution	Cu, grams per litre.	NH_3, grams per litre.
A.	11·8	195·3
1st dilution	11·6	150·5
2nd ,,	11·0	132·5
3rd ,,	10·4	119·6
4th ,,	8·9	99·1
5th ,,	7·4	85·1
6th ,,	6·4	72·8
7th ,,	5·2	63·7
8th ,,	4·6	56·4
9th ,,	2·9	38·0
10th ,,	1·3	22·5
B.	12·2	205·2
1st dilution	12·1	176·4
2nd ,,	11·6	147·2
3rd ,,	9·6	112·8
4th ,,	7·8	95·9
5th ,,	6·4	77·7
6th ,,	5·2	60·8
7th ,,	4·0	46·2

The solubility of tetrammine copper sulphate in ammonia is a definite figure, since this substance is a definite crystalline compound, but the solubility of copper hydroxide seems to depend on the method of preparation adopted, and unless great precautions are taken, slight variations may be obtained even when one method of preparation is used, giving slightly variable solubility figures.

If the basic copper sulphate obtained by Ost's method behaves, on treatment with ammonia, as tetrammine copper sulphate and copper hydroxide, there will be a definite solubility of the tetrammine copper sulphate in ammonia of any particular strength and a solubility of copper hydroxide, which may vary owing to variations in the conditions of preparation of the basic copper sulphate. The use of an excess of basic copper sulphate should, therefore, give a solution in ammonia saturated with respect to tetrammine copper sulphate and with respect to copper hydroxide.

This was tested quantitatively in the following manner. A large excess of basic copper sulphate obtained by Ost's method was added to ammonia (D 0·880), and the whole kept in a thermostat at 15° in a tightly stoppered bottle for twenty-four hours and well shaken at intervals. The content of copper and ammonia in solution was then estimated. Additions of distilled water were then

made, and after each addition the solution was shaken at 15° for twenty-four hours before estimating the copper and ammonia again. Two sets of experiments were carried out, and the results were as follows:

Solution.	Cu, grams per litre.	NH_3, grams per litre.
Original No. 1	11·0	267·1
After 1st dilution..........	11·8	247·5
" 2nd "	12·6	237·2
" 3rd "	13·3	228·4
" 4th "	15·7	207·0
" 5th "	17·8	192·2
" 6th "	19·4	182·0
" 7th "	23·3	145·6
" 8th "	26·4	129·7
Original No. 2.	11·3	237·8
After 1st dilution..........	13·5	218·0
" 2nd "	14·6	206·7
" 3rd "	16·7	194·4
" 4th "	17·4	181·5
" 5th "	17·6	171·7

The results obtained are not quite coincident, indicating the existence of different modifications of the basic copper salt, but the differences are scarcely larger than those obtained in the determination of the solubility of copper hydroxide in ammonia. This experiment confirms the impossibility of obtaining constant solutions by Ost's method, owing to the variation in solubility of copper hydroxide in ammonia.

If the solubility curves of basic sulphate, tetrammine copper sulphate, and cupric hydroxide are considered together, it will be seen (Fig. 3) that the solubility curve for basic copper sulphate represents a solution saturated with both tetrammine copper sulphate and copper hydroxide, the solubility being the sum of the solubility of tetrammine copper sulphate and of the solubility of some modification of copper hydroxide, as the general form of the curve and the value of the solubility found is consistent with this view.

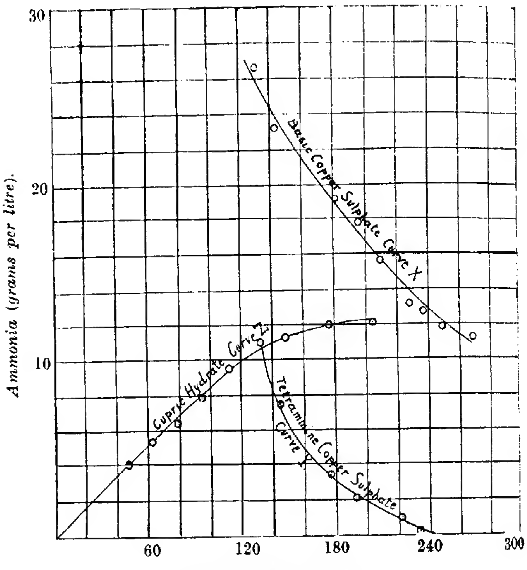
The study of Ost's cuprammonium solution described above rendered it evident that the precise adjustment of this solution to definite concentration of copper and ammonia would be difficult, and as it was apparent that the value of the viscosity obtained for a sample of cotton depended to an appreciable extent on the concentration of ammonia and copper in the solution, Ost's method of preparation of the solution was abandoned.

Since copper hydroxide prepared by Dawson's method showed a fairly definite solubility in ammonia, an unsaturated solution of this form of copper hydroxide was chosen as the standard cuprammonium solution.

The method adopted was the following. Sixty grams of copper sulphate are dissolved in 1 litre of hot water, a few drops of sulphuric acid added, the solution is allowed to cool to 50°, and ammonia (D 0·880) added until the precipitation of basic copper sulphate is complete, any excess of ammonia being neutralised with a few drops of sulphuric acid. The precipitated basic sulphate is allowed to settle, and the supernatant liquid decanted.

FIG. 3.

Solubilities in ammonia at 15°.



The precipitate is washed by decantation with hot water, 200 c.c. of 20 per cent. sodium hydroxide solution are added, and the whole is well shaken at the ordinary temperature. The precipitate is converted into blue cupric hydroxide, which is then allowed to settle, the supernatant liquid decanted, and the precipitate washed by decantation with cold water until the filtrate is free from alkali and sulphate. The precipitate is then collected, washed with distilled water, and dried on a porous plate at 40°.

The dried cupric hydroxide is transferred to an aspirator bottle and 800 c.c. of ammonia, containing 200—210 grams of ammonia per litre, are added. The whole is well shaken and the excess of cupric hydroxide allowed to settle. The supernatant liquid is run off through a glass wool filter and the volume measured. The copper in the solution is determined, and the theoretical quantity of ammonia is added to give a solution containing 11 grams of copper and 200—210 grams of ammonia per litre.

The composition of the finished solution is finally checked by analysis.

Trouble may be experienced in preparing this solution unless the conditions laid down are strictly maintained.

This work was carried out at the Research Department, Royal Arsenal, Woolwich, and is published by permission of the Director of Artillery, War Office, to whom our thanks are due. We also desire to express our thanks to Lieut.-Colonel R. A. Craig. C.M.G., and to Sir Robert Robertson, K.B.E., F.R.S., for the interest they have shown in this work.

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LIII.—*The Influence of the Solvent on the Velocity of Reaction between certain Alkyl Iodides and Sodium β-Naphthoxide.*

By Henry Edward Cox.

From the literature relating to the influence of the solvent on velocity of reaction, it is apparent that no satisfactory connexion between the physical or chemical properties of the solvent and its effect on velocity-constants has yet been deduced. Theories which are in agreement with the observations in one reaction are found to be quite at variance with facts when the same solvents are examined in relation to another reaction.

The most obvious supposition, based on the Nernst-Thomson rule, that the velocity would be greatest in solvents of highest dielectric constant, is satisfactory in the case of certain reactions investigated by Menschutkin (*Zeitsch. physikal. Chem.*, 1887, **1**, 611; 1890, **6**, 41), but it is quite useless in the case of a large

number of other reactions, even those in which the reaction is probably between ions.

A comprehensive theory by van't Hoff ("Vorlesungen," 1901, 1, 214), in which the action of the solvent is attributed to displacement of the equilibrium of the reacting system—depending on solubility relations—and a possible specific effect, has been found to be in accord with the facts in certain isomeric changes investigated by Dimroth (*Annalen*, 1910, **377**, 127), but attempts to apply it to other reactions fail. It is therefore evident that specific catalytic effects quite outweigh the effects of displacement of equilibrium.

There is also no evidence that viscosity of the solvent has any great influence on the velocity-constants; experiments by Reformatsky (*Zeitsch. physikal. Chem.*, 1891, **7**, 34) and others show that velocity is not decreased by increasing viscosity.

The only generalisation that appears to be supported by most of the available data is that of Patterson and Montgomerie (T., 1912, **101**, 26, 2100), who state that "it appears that solvents influence quite different reactions in a uniform manner; although the manifestation of this effect may be of an opposite character, a given set of solvents may hasten a particular reaction in a certain sequence, whilst in the same, or nearly the same, sequence they retard another reaction. The property or properties which bring this about are probably the same throughout."

Several examples of this are to be found in the literature, and some are quoted by Patterson and Montgomerie. It is considered by several authorities that in many or all cases some combination occurs between solvent and solute, with the formation of additive compounds of an unstable kind. On the radiation theory (compare Baly, "Spectroscopy," 1918, 491), this gives rise to a field of force in the surrounding ether, which is opened by the absorbable radiation, with consequent increase in chemical activity.

On these views, it is not unreasonable to expect that there might be some connexion between the chemical constitution of a solvent and its effect on the velocity of any particular reaction. It is therefore of interest to examine the influence of a series of related solvents in the hope of tracing some connexion between the constitution and the effect on the velocity. For the particular reactions here discussed, the alcohols form a convenient series from considerations of solubility.

The velocity-constants of the reactions between methyl, ethyl, and *n*-propyl iodides and sodium β-naphthoxide have therefore been measured in the following fifteen alcohols: methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec.*-, and *tert.*-butyl, *n*-, *iso*-, *sec.*-, and *tert.*-

amyl, allyl and benzyl alcohols, and ethylene glycol (as an example of a dihydric alcohol). The influence of concentration has been measured in four of them, and the effect of water has been studied. The alcohols afforded opportunity of observing the effect of structure in the different isomerides as well as the regular effect of increasing molecular weight in a homologous series. No complication arises except the possible alcoholysis discussed below and the increasing constant in the case of *tert.*-amyl alcohol. Sodium β-naphthoxide is readily soluble in the alcohols, but it is only very sparingly so in neutral or acidic solvents of the associating type. No results appear on record for a series of alcohols or other homologous series, although a number of observations are recorded on ethyl, methyl, *iso*butyl, and benzyl alcohols; these are often in the same increasing or decreasing order as stated by Patterson and Montgomerie.

Some account of the reaction between the alkyl iodides and sodium naphthoxides has been given in previous papers (T., 1918, **113**, 666, 821), and it has been shown that the reactions are bimolecular, but that the constant is dependent on the initial concentration. In a series of solvents here described, the reaction has been found to be regular in all cases, and satisfactory values of the velocity-constant are obtained.

In *tert.*-butyl and *tert.*-amyl alcohols, however, there is a gradual increase in the value of k for methyl iodide as the reaction proceeds, so that it is necessary to measure only a small part of the reaction to obtain a satisfactory constant. This is apparently due to the low solubility of the products of the reaction, which are precipitated after a short time, the velocity of reaction then increasing.

EXPERIMENTAL.

The Influence of the Solvent on the Velocity of Reaction at 50·5°.

The method of preparation of sodium β-naphthoxide given in the previous paper has been improved. Sodium is dissolved in recently boiled absolute alcohol, the calculated quantity of dry β-naphthol added, and the solution evaporated to dryness in a vacuum. The product is dissolved in the smallest possible quantity of boiling acetone; the flask is corked while the solution is still boiling, and immediately cooled; the salt then crystallises in minute lamellæ ($C_{10}H_7ONa,C_3H_6O$), and is filtered rapidly, washed with cold acetone, then dried at 150° in a current of hydrogen. Sodium β-naphthoxide obtained in this way is quite white.

The method of measuring the velocity was the same as before, special pipettes being made to work with very small quantities of

the more expensive solvents. In each experiment the initial concentration is N with respect to naphthoxide and iodide, and the temperature is 50·5°.

The values of k are in good agreement in each experiment, and in many cases duplicate determinations have been made. For economy of space, only a few typical experiments will be given in full, and the other results summarised. The unit of time is one minute and of concentration one gram-molecule per litre.

Normal Primary Alcohols.

Methyl, ethyl, and n-propyl alcohols were in each case dehydrated over calcium oxide and calcium, and finally distilled from fresh calcium turnings. n-Butyl alcohol was fractionated several times from "fermentation" butyl alcohol, then dehydrated with potassium carbonate and, finally, quicklime, and again fractionated. It boiled at 116—116·5°/756 mm. n-Amyl alcohol was from Kahlbaum.

n-Propyl Alcohol.

N-Ethyl iodide; N-Naphthoxide. 0·500 C.c. titrations, $N/25$-HCl.

t.	$a-x$.	k.
0	11·70	—
9	10·55	0·0129
16	9·80	0·0127
24	9·10	0·0127
32	8·40	0·0131
41	7·95	0·0123
	Mean	0·0127
	(Duplicate	0·0129).

n-Butyl Alcohol.

N-Methyl iodide; N-Naphthoxide; 0·500 C.c. titrations, $N/25$-HCl.

t.	$a-x$.	k.
0	10·65	—
3	9·40	0·0520
6	8·40	0·0524
9	7·60	0·0523
12	6·85	0·0542
15	6·35	0·0530
	Mean	0·0528.

TABLE I.

Summary of Results.

Solvent.	Methyl iodide.	Ethyl iodide.	n-Propyl iodide.
Methyl alcohol	0·0459	0·0130	0·00567
Ethyl alcohol	0·0941	0·0212	0·00859
n-Propyl alcohol	0·0643	0·0127	0·00507
n-Butyl alcohol	0·0528	0·0107	0·00379
n-Amyl alcohol	0·0298	0·00518	0·00194

On consideration of the above results for normal alcohols, it is apparent that, with the exception of methyl alcohol, which is subnormal, there is a gradual and fairly regular decrease in the value of k with increasing molecular weight; this is well shown on plotting a curve, velocity-constant–molecular weight (see Fig. 1). This suggests that the influence is partly additive as well as a

constitutive property, as the addition of a CH_2-group has a regular retarding action, which somewhat diminishes as the series is ascended.

There is a striking similarity in this curve to that of Burke and Donnan (T., 1904, **85**, 555), who, in their investigation of the reaction between silver nitrate and alkyl iodides, found a similar effect of the methyl group in the activity of the iodides, and this goes to show that methyl alcohol is subnormal in its action as solvent; its normal position should be far above ethyl alcohol (compare the curves given for Menschutkin's and Hecht and Conrad's data by Segaller, T., 1913, **103**, 1154).

It may be remarked that in a large number of reactions recorded the velocity in ethyl is greater than in methyl alcohol, and the opinion is expressed by Senter (T., 1916, **109**, 686) that, in general, reactions should be faster in methyl alcohol, which he attributes to the higher viscosity of ethyl alcohol.

In a number of other reactions, however, methyl alcohol is the more favourable medium, and the above results suggest that this subnormal activity in certain reactions may be one of the frequently observed irregularities of the first member of a homologous series. Sodium ethoxide, phenoxide, and α- and β-naphthoxides all react more rapidly in ethyl alcohol.

Although the influence of these solvents is similar in each case, there are minor differences; thus, it appears from the following tables of the relative values in the solvents that the three iodides are not affected equally; ethyl and *n*-propyl iodides are more affected than is methyl iodide.

This is shown in table II by expressing the velocities in terms of the velocity in *n*-amyl alcohol.

TABLE II.

Solvent.	Methyl iodide.	Ethyl iodide.	*n*-Propyl iodide.
Methyl alcohol	1·54	2·51	2·92
Ethyl alcohol	3·16	4·09	4·43
n-Propyl alcohol	2·16	2·45	2·61
n-Butyl alcohol	1·77	2·06	1·95
n-Amyl alcohol	1·00	1·00	1·00

The differences become more marked in some of the other solvents dealt with in this paper.

iso-, sec.-, *and* tert.-*Alcohols.*

*iso*Propyl, *sec.*-amyl (methylpropylcarbinol), and *tert.*-butyl alcohols were Kahlbaum's preparations dehydrated over quicklime.

*iso*Butyl alcohol was fractionated from the commercial product and boiled at 107·5—109°; *sec.*-butyl alcohol was prepared by a Grignard reagent and boiled at 99·5—100·5°. *iso*Amyl alcohol was purified from *sec.*-butylcarbinol by preparing potassium amyl sulphate and crystallising; after dehydrating, it distilled at 131—132°, and had $[\alpha]_D^{15}$ less than 0·5°. *tert.*-Amyl alcohol was prepared by Adams, Kamm, and Marvel's method (*J. Amer. Chem. Soc.*, 1918, **40**, 1950), and boiled at 102—103°.

The results of the velocity experiments are all in satisfactory agreement, as illustrated below, with the exception that, in *tert.*-butyl and *tert.*-amyl alcohols, methyl iodide shows a gradual increase, due, apparently, to insolubility of the naphthyl methyl ether; these figures are given in the examples below:

sec.-*Propyl Alcohol.*

N-Propyl iodide; *N*-Naphthoxide. 0·500 C.c. titrations, *N*/25-HCl.

t.	*a*−*x*.	*k*.
0	12·00	—
21	10·65	0·00629
34	9·95	0·00631
51	9·25	0·00607
64	8·70	0·00617
75	8·30	0·00619
	Mean *k*.........	0·00621

Methylpropylcarbinol.

N-Methyl iodide; *N*-Naphthoxide. 0·112 C.c. titrations, *N*/100-HCl.

t.	*a*−*x*.	*k*.
0	10·50	—
2	9·90	0·0323
5	9·15	0·0315
8	8·50	0·0314
11	7·65	0·0361
14	7·20	0·0349
	Mean *k*.........	0.0332

tert.-*Butyl Alcohol.*

N-Methyl iodide: *N*-Naphthoxide. 0·112 C.c. titrations, *N*/100-HCl.

t	*a*−*x*.	*k*.
0	10·40	—
3	9·50	0·0341
7	8·65	0·0311
9	7·85	0·0389
12	6·85	[0·0465] omitted.
0	10·45	—
5	9·20	0·0325
8	8·40	0·0365
10	8·00	0·0366
	Mean *k*	0·0352

tert.-*Amyl Alcohol.*

N-Methyl iodide; *N*-Naphthoxide. 1·00 C.c. titrations, *N*/25-HCl.

t.	*a*−*x*.	*k*.
0	24·50	—
20	20·20	0·0109
27	19·05	0·0108
34	17·50	0·0120
40	16·70	0·0119
	Mean *k*	0·0114

The results obtained in these alcohols are summarised below.

TABLE III.

Solvent.	Methyl iodide.	Ethyl iodide.	Propyl iodide.
*iso*Propyl Alcohol	0·0975	0·0177	0·00621
*iso*Butyl ,, ...	0·0635	0·0113	0·00374
sec.-Butyl ,, ...	0·0571	0·0107	0·00370
tert.-Butyl ,, ...	0·0350	0·00501	0·00149
*iso*Amyl ,, ...	0·0392	0·00649	0·00199
sec.-Amyl ,, ...	0·0332	0·00461	0·00167
tert.-Amyl ,, ...	0·0114	0·00155	0·000525

These results show the same diminution of the velocity-constant as the series is ascended in the same class of alcohol; thus, the velocity decreases regularly in the series *iso*propyl, *iso*butyl, *iso*amyl, similarly with the series of secondary and tertiary alcohols.

This is clearly seen in Fig. 1, which shows the *iso*-alcohols; the effect of increasing molecular weight is very similar in the four classes of alcohols. It is also apparent from the table of results or the figures that the *iso*-alcohols are in each case more favourable media than their normal isomerides; similarly, the secondary alcohols are more favourable solvents than the tertiary alcohol of the same molecular weight, but are slightly less active than the corresponding *iso*-alcohol. For a given molecular weight, therefore, the order of decreasing activity is: *iso*, secondary, normal, tertiary. Thus, with methyl iodide the figures are:

*iso*Butyl alcohol	0·0635	*iso*Amyl alcohol	0·0392
sec.-Butyl alcohol	0·0571	*sec.*-Amyl alcohol......	0·0332
n-Butyl alcohol	0·0528	*n*-Amyl alcohol	0·0298
tert.-Butyl alcohol......	0·0350	*tert.*-Amyl alcohol......	0·0114

(In the reaction with ethyl and *n*-propyl iodides the figures are very near together in the amyl alcohols, and there appears to be a small divergence from this order.)

In connexion with these results, the following points may be noted. In all three classes of alcohols, the increasing number of carbon atoms in a straight chain decreases the activity as solvent; a branching chain in the primary alcohols produces a distinct rise in activity, so much so that the constant approximates to that of the next higher normal primary alcohol. The introduction of a methyl group into the carbinol group produces, first, a rise (secondary alcohols) and then a larger fall (tertiary alcohols).

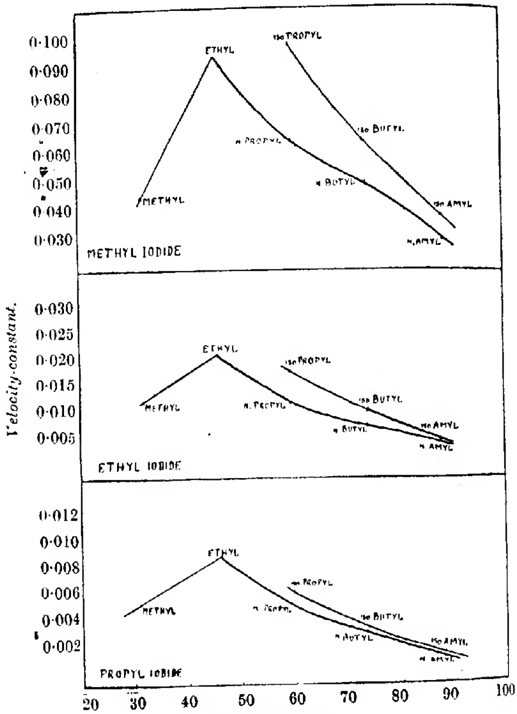
It may be remarked that these observations are in the opposite order to the activity of the corresponding alkyl iodides as measured by velocity of etherification with sodium phenoxide (Segaller, *loc. cit.*), it having been found that *iso*- and *sec.*-alkyl iodides are less

reactive than the normal isomerides, and tertiary iodides much more reactive.

Allyl and Benzyl Alcohols and Ethylene Glycol.

These alcohols have been included specially to observe the effect of unsaturation, a benzene ring, and a second hydroxyl group respectively. The reaction in these solvents is quite normal.

FIG. 1.



Molecular weight.

Normal and iso-*alcohols.*

On account of the high viscosity of glycol, a special pipette was calibrated with no constriction at the outlet; it was rinsed out

each time with water; in this way, the quantity delivered is satisfactorily constant.

Allyl alcohol was distilled from calcium oxide immediately before use (b. p. 94—95°). Benzyl alcohol was the commercial product redistilled three times (b. p. 205·5°), and ethylene glycol was prepared in the usual way from ethylene dibromide; it boiled at 197°. The experimental data are exemplified by the reaction with ethyl iodide in glycol:

N-Ethyl iodide. 0·129 C.c. titrations.		*N*-Naphthoxide. *N*/100-HCl.
t.	*a*−*x*.	*k*.
0	12·40	—
15	10·25	0·0145
23	9·45	0·0141
30	8·90	0·0136
40	8·00	0·0143
	Mean *k*	0·0141

In the case of methyl and ethyl iodides, the mixture is homogeneous up to about one-half the reaction, after which time the ether begins to separate out. With propyl iodide, the reaction proceeds to about two-thirds before separation of the products.

TABLE IV.

Summary of Results in these Solvents.

Solvent.	Methyl iodide.	Ethyl iodide.	Propyl iodide.
Allyl alcohol	0·0381	0·00562	0·00195
Benzyl alcohol	0·0357	0·00781	0·00242
Ethylene glycol..........	0·0578	0·0141	0·00431

It is remarkable that the velocity-constants are of similar magnitude in three such different solvents; the figures are quite comparable with propyl and amyl alcohols, already discussed.

Allyl alcohol was specially selected because of its well-known similarity in physical properties to *n*-propyl alcohol, and the fact that the constants are distinctly different (about one-half) from those in the latter solvent is very suggestive that the solvent influence is largely chemical rather than physical; the boiling point, dielectric constant, and refractive index (which is important from the point of view of the radiation hypothesis) are almost identical, yet the introduction of a double bond makes more difference in the velocity than there is between *n*- and *iso*-propyl alcohols. This supports the idea that the solvent participates in a chemical reaction.

A comparison of the figures for benzyl alcohol brings out the

fact that the velocity-reducing effect of a number of carbon atoms when in the form of the benzene ring is less than that of a similar number in a straight chain, for the value of k is somewhat higher than that of *n*-amyl alcohol with four carbon atoms attached in a chain to the carbinol group. It may be remarked, too, that in much work in which benzyl alcohol has figured it is a more favourable medium than some of the aliphatic alcohols, notably *iso*amyl alcohol.

Ethylene glycol illustrates the effect of a second hydroxyl group; on comparing it with ethyl alcohol, it is seen that the exchange of hydrogen for hydroxyl considerably reduces the activity of the solvent, and its effect is not much different from *n*-propyl alcohol, so that the introduction of a hydroxyl group is similar in result to the introduction of another CH_2-group.

There is, however, nothing to show the influence of solubility, which is so different in glycol and ethyl alcohol.

Influence of Water on the Velocity of Reaction.

Water should take the first place in a list of alcohols, but it is not possible to measure the velocity of these reactions in it, because the alkyl iodides are not sufficiently soluble, but the effect of water on the velocity has been found to be very considerable in many reactions. For this reason, the effect of water on the velocity of the reaction with ethyl iodide in ethyl alcohol has been investigated, with the following results:

TABLE V.

Ethyl Alcohol.

Percentage by weight.	k.
100	0·0212
90	0·0227
80	0·0255
70	0·0241
60	0·0206

In 50 per cent. alcohol, the naphthyl ethyl ether separates early in the reaction, and the velocity at once increases; below 50 per cent., the alkyl iodide is not soluble to N-concentration. It is seen from these results that the addition of water at first accelerates the reaction, a maximum being reached in the vicinity of 80 per cent. alcohol; thereupon the further addition of water retards the velocity.

It may be remarked that Miss Burke and Donnan made a similar observation with silver nitrate (*Zeitsch. physikal. Chem.*, 1909,

69, 163). No explanation has been suggested, but it is possible that side reactions take place in the case of aqueous-alcoholic sodium naphthoxide, as this substance undergoes hydrolysis in water and probably alcoholysis in ethyl alcohol.

The Influence of the Solvent on the Relative Activity of the Alkyl Iodides, and Comparison of Sodium Ethoxide, Phenoxide, and Naphthoxide.

The previous pages show that there is no inversion of the order of activity of the three alkyl iodides by influence of the solvent, but it is noticeable that the order of the activity of the solvents is not quite the same. Table VI shows the relative activity in the above solvents in terms of the slowest (namely, *tert.*-amyl alcohol), and columns 4, 5, and 6 show the relative activity of the three iodides in each solvent in terms of propyl iodide in that solvent. For example, it is seen that methyl iodide is from eight to twenty-four times as reactive as propyl iodide, according to the solvent, and the influence of the solvent is greater on propyl iodide than on methyl iodide.

TABLE VI.

Solvent.	Methyl iodide.	Ethyl iodide.	Propyl iodide.	Methyl iodide.	Ethyl iodide.	Propyl iodide.
*iso*Propyl alcohol	8·55	11·41	11·84	15·70	2·85	1·00
Ethyl „	8·25	13·69	16·38	10·95	2·47	1·00
n-Propyl „	5·64	8·20	9·65	12·68	2·50	1·00
*iso*Butyl „	5·57	7·30	7·13	16·96	3·02	1·00
Glycol	5·07	9·10	8·21	13·41	3·27	1·00
sec.-Butyl „	5·01	6·90	7·05	15·45	2·90	1·00
n-Butyl „	4·63	6·90	7·22	13·93	2·82	1·00
Methyl „	4·02	8·39	10·80	8·13	2·29	1·00
*iso*Amyl „	3·44	4·18	3·79	19·70	3·26	1·00
Allyl „	3·34	3·63	3·72	19·54	2·88	1·00
Benzyl „	3·13	5·04	4·61	14·75	3·23	1·00
tert.-Butyl „	3·07	3·23	2·84	23·49	3·36	1·00
sec.-Amyl „	2·91	2·98	3·18	19·88	2·76	1·00
n-Amyl „	2·62	3·34	3·70	15·37	2·67	1·00
tert.-Amyl „	1·00	1·00	1·00	21·71	2·95	1·00

In ethyl alcohol as solvent, it is possible to compare the activity of sodium ethoxide, phenoxide, and naphthoxide, as these have all been measured with the alkyl iodides (Hecht Conrad and Brückner, and Segaller); the figures for ethoxide and phenoxide are calculated from the data of these authors. At 42·5°, the relative activity of β-naphthoxide as compared with phenoxide is:

Methyl iodide	1·4
Ethyl „	1·4
Propyl „	1·5

which shows that the relative activity of these bases is constant and independent of the iodide with which it is measured. The following figures show that when ethoxide is compared with phenoxide and naphthoxide, the activity is not independent of the iodide.

(t = 40·0°).	$\frac{\text{Ethoxide}}{\beta\text{-Naphthoxide}}$.	$\frac{\text{Ethoxide}}{\text{Phenoxide}}$.
Methyl iodide	5·3	7·4
Ethyl ,, ...	1·9	2·7
Propyl ,, ...	1·5	2·2

The Effect of Initial Concentration in Various Solvents.

In the previous papers already referred to, it has been shown that the velocity of reaction of the alkyl iodides with sodium naphthoxide is dependent on the initial concentration of the base. In ethyl alcohol, the velocity has been shown to be decreased in accordance with Hecht and Conrad's equation, $k_v = k_1 + a \log v$.

The work of Acree and his co-workers (see Shroder and Acree, T., 1914, **105**, 2582) shows that sodium ethoxide and phenoxide are very much ionised in alcoholic solution, and that both the ions and the molecules take part in the reaction with alkyl iodides, and that with different velocities.

It is reasonable to suppose that a similar phenomenon takes place with naphthoxide (boiling-point determinations by the author show evidence of dissociation), which makes it probable that this increase is due to the increasing ionisation, and, consequently, increasing proportion of the reaction due to ions instead of molecules. It has also been shown that at higher dilutions the velocity-constant increases abnormally rapidly with methyl iodide in ethyl alcohol.

A similar increase—first regular, then abnormal—is now observed in methyl alcohol, and it is convenient to discuss these two solvents separately, because in them the question of alcoholysis arises, and

TABLE VII.

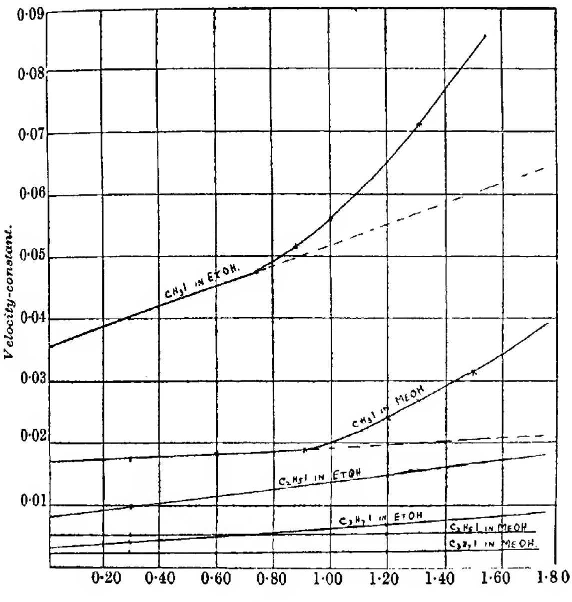
Methyl Iodide and Sodium β-Naphthoxide in Equivalent Concentration. $t = 40·0°$.

v.	k_v (found).	k_v (calculated).
1	0·0164	0·0164
2	—	0·0171
4	0·0179	0·0179
8	0·0183	0·0186
16	0·0242	0·0194
32	0·0313	0·0201
64	0·0369	0·0209

"a" = 0·0025.

experiments have been made with a view to gain information on this point. The results obtained for the three iodides and sodium β-naphthoxide in methyl alcohol are shown in tables VII and VIII and illustrated in Fig. 2. It will be seen that the same phenomena appear in both these solvents; the figures in ethyl alcohol have already been given (T., 1918, **113**, 666).

FIG. 2.



Sodium β-naphthoxide and the alkyl iodides in methyl and ethyl alcohols.

TABLE VIII.

	Ethyl Iodide.		*Propyl Iodide.*	
v.	k_v (found).	k_v (calc.).	k_v (found).	k_v (calc.).
1	0·00460	0·00460	0·00202	0·00202
4	0·00293	0·00496	0·00233	0·00238
16	0·00539	0·00532	0·00277	0·00274
32	0·00551	0·00550	0·00299	0·00292
	"a" = 0·00060		"a" = 0·00060.	

The figures are very similar to those obtained for sodium α-naphthoxide; the latter, however, is slightly more reactive; thus, at N-concentration in methyl alcohol, k_α/k_β is:

Methyl iodide..................	1·00
Ethyl iodide	1·16
Propyl iodide..................	1·17

The work of Acree and others in connexion with sodium ethoxide and phenoxide shows that the velocity increases with decreasing concentration, because the reaction is between ions and molecules of the base and the non-ionised alkyl iodide; the velocity of the ionic reaction is greater than that of the molecular reaction, so that as the ionisation increases with dilution, so does the velocity increase. Shroder and Acree show, in the paper already quoted, that the increase of ionisation is according to the empirical equation of Hecht and Conrad.

In considering the cause of the abnormal increase in activity of methyl iodide at higher dilutions in both methyl and ethyl alcohols, it is to be expected that if it were due to a property of the naphthoxide, it would appear also with the other alkyl iodides. Some evidence has been obtained which suggests that sodium β-naphthoxide undergoes alcoholysis in dilute solution, and this hypothesis affords an explanation of the phenomena observed, but, owing to the experimental difficulty of detecting traces of ethyl ether in a complex alcoholic mixture, conclusive evidence has not been obtained.

The formation of ether is possible in two ways: (1) by alcoholysis, in which case the reactions are: (*a*) $C_{10}H_7{\cdot}ONa + EtOH \rightleftharpoons C_{10}H_7{\cdot}OH + EtONa$; (*b*) $EtONa + EtI \longrightarrow Et_2O + NaI$; (2) by alkylidene dissociation (alkylene dissociation is impossible with methyl iodide).

The latter possibility (Nef, *Annalen*, 1899, **309**, 126) has been critically examined by Miss Burke and Donnan (T., 1904, 85, 555), and shown to be unsatisfactory; also, if it occurred with naphthoxide, it would be expected with phenoxide, ethoxide, and other bases.

The velocity of reaction between sodium ethoxide and the alkyl iodides is greater than that of sodium naphthoxide, so that if alcoholysis takes place, a higher value of k will be obtained at the commencement of a reaction than at the end, when the increasing concentration of free naphthol retards further alcoholysis. In this case, the effects would be expected in the case of each of the three alkyl iodides, but examination of the velocity-constants shows that a small amount of alcoholysis would not be detected in this way The following table shows the velocity-constants of methyl,

ethyl, and propyl iodides with sodium ethoxide at 40·0° (solvent, ethyl alcohol), calculated from the data of Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289).

TABLE IX.

	Methyl iodide.		Ethyl iodide.		Propyl iodide.	
	Ethoxide.	Naphth-oxide.	Ethoxide.	Naphth-oxide.	Ethoxide.	Naphth-oxide.
1	0·188	0·0356	0·0148	0·00790	0·00483	0·00316
2	0·214	0·0406	0·0175	0·00991	0·00597	—
5	0·248	0·0473	0·0211	0·0116	0·00747	0·00536
10	0·273	0·0559	0·0238	0·0140	0·00841	0·00653
20	0·299	0·0721	0·0265	0·0157	0·00971	0·00739
40	0·323	—	0·0292	0·0170	0·01089	0·00852

The constants for methyl iodide and ethoxide are five times greater than those of sodium β-naphthoxide and the same iodide, but those with ethyl and propyl iodides with ethoxide are only 1·7 and 1·5 times the corresponding figures with naphthoxide. As the values are so nearly the same with the latter iodides, it is clear that a very small amount of ethoxide produced by alcoholysis would produce so small a change in the value of k that its effect would not be observed.

The following experiments show the effect of sodium ethoxide on the reaction; the amount added is larger than that likely to be produced by alcoholysis.

Experiment 1.—Solvent, ethyl alcohol, $t = 40·0°$, $N/8$-methyl iodide, $N/10$-sodium naphthoxide, $N/40$-sodium ethoxide.

Experiment 2.—Solvent, ethyl alcohol, $t=40·0°$, $N/8$-ethyl iodide, $N/10$-sodium naphthoxide, $N/40$-sodium ethoxide (these are equivalent to $N/8$-ethoxide and $N/10$-β-naphthol). Acid = $N/25$-HCl, 5·0 c.c. titrations.

1.

t.	$a-x$.	k.	k'.
0	15·25	—	—
10	13·75	0·0894	0·0894
25	12·10	0·0854	0·0826
42	11·00	0·0792	0·0689
62	9·85	0·0725	0·0604
102	8·50	0·0638	0·0503
150	7·30	0·0595	0·0503

2.

t.	$a-x$.	k.	k'.
0	15·55	—	—
62	13·75	0·0170	0·0170
120	12·50	0·0164	0·0157
180	11·40	0·0163	0·0161
284	9·95	0·0159	0·0154
363	9·05	0·0159	0·0158
440	8·35	0·0158	0·0151
	Mean	0·0162	

Experiment 3.—Solvent, methyl alcohol, $t=40·0°$, $N/8$-methyl iodide, $N/10$-sodium naphthoxide, $N/40$-sodium methoxide. Acid = $N/30$-HCl, 5·0 c.c. titrations.

t.	$a-x$.	k.	k'.
0	18·55	—	—
17	17·40	0·0286	0·0286
33	16·60	0·0288	0·0288
54	15·65	0·0276	0·0261
85	14·50	0·0266	0·0246
115	13·65	0·0262	0·0214
145	12·90	0·0245	0·0212

In these experiments, the figures in the fourth column (k') are obtained by calculation from each pair of titrations; this shows the course of the reaction and the decrease in k more clearly than the figures in the third column, which are referred to t_0 in the usual way. Experiments 1 and 3 show a similar course in both methyl and ethyl alcohols. At the commencement of the reaction, k is much increased (nearly doubled in ethyl alcohol), and rapidly diminishes as the free ethoxide is used up; then it falls to a value approximating that of $N/10$-naphthoxide. In Experiment 2, the course of the reaction with ethyl iodide is seen; here the presence of ethoxide has no apprecable effect on the velocity-constant after the first titration, and even in that the effect is not large. These experiments show that alcoholysis increases the mean velocity-constant with all the iodides, but that a small amount of alcoholysis does not show a marked diminution in k as a reaction proceeds, and is so small that with the higher alkyl iodide its effect would be unnoticeable. It is therefore suggested that in dilute alcoholic solution, sodium naphthoxide undergoes alcoholysis to a small extent, and this occasions the observed increase with methyl iodide at high dilutions.

Further experiments were made with the object of detecting ethyl ether in the products of the reaction; in the author's opinion ether was present, but owing to the experimental difficulty it has not been definitely proved.

The influence of initial concentration has also been measured in *iso*butyl and benzyl alcohols. In these solvents, the effect is very large; in the case of ethyl and propyl iodides, the velocity is nearly doubled by changing the initial concentration from N to $N/8$, yet, as will be seen from the examples already given, there is no important rise in the velocity-constant during any one experiment, although in many cases more than half the reaction was measured. It may be suggested that the negative catalytic effect of the product of the reaction may just balance the increasing velocity due to the decreasing concentration of the reacting substances.

*iso*Butyl and benzyl alcohols are much more associated substances than methyl and ethyl alcohols, and it may be that the

reacting ions or molecules are associated with the solvent molecules. The experimental results are as follows.

TABLE X.

	Methyl iodide.		Ethyl iodide.		Propyl iodide.	
v.	*iso*Butyl.	Benzyl.	*iso*Butyl.	Benzyl.	*iso*Butyl.	Benzyl.
1	0·0232	0·0125	0·00399	0·00273	0·00135	0·000884
4	0·0263	0·0212	0·00615	0·00393	0·00245	0·00216
8	0·0291	0·0267	0·00756	0·00647	0·00284	0·00329

In the light of Acree's work, the fact that k changes with dilution is strong evidence that the reaction in these solvents also is one between ions and molecules jointly.

Summary.

In the hope of tracing some relation between the constitution of a solvent and its effect on the velocity of a particular reaction, the velocity of reaction between sodium β-naphthoxide and methyl, ethyl, and *n*-propyl iodides has been measured at 50·5° in *N*-concentration in methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec.*-, and *tert.*-butyl, *n*-, *iso*-, *sec.*-, and *tert.*-amyl, allyl, and benzyl alcohols, and ethylene glycol.

It has been found that some relation does exist for these reactions and solvents. The velocity in the *n*-, *iso*-, *sec.*-, and *tert.*-series steadily decreases with increasing molecular weight, with the exception of the anomalous behaviour of methyl alcohol, which is a less favourable solvent than ethyl alcohol. For alcohols of a given molecular weight, the order of decreasing activity is *iso*-, *sec.*-, *n*-, *tert.*-, and is independent of the alkyl iodide.

Allyl alcohol does not compare closely with *n*-propyl alcohol, with which it is physically similar; the effect of the unsaturated group is to decrease the velocity. Benzyl alcohol is a more favourable medium than a straight-chain alcohol of the same molecular weight, and the velocity in ethylene glycol is lower than that in ethyl alcohol, showing that the displacement of a hydrogen atom by a hydroxyl group reduces the velocity. The addition of water to ethyl alcohol at first increases the velocity to a maximum at about 80 per cent. of alcohol, and then retards the reaction.

It is suggested that these facts support the idea that a solvent participates in the reaction, and its physical properties have only a subordinate influence.

The order of the activity of the alkyl iodides is only approxim-

ately independent of the solvent, and the relative activities of the iodides are dependent on the solvent.

The ratio of the activity of sodium phenoxide and naphthoxide is independent of the alkyl iodide, but the ratio of naphthoxide to ethoxide is not so independent.

The influence of initial concentration has also been studied in four solvents. In each case there is an increase in velocity with decreasing initial concentration. In the cases of methyl and ethyl alcohols, evidence is adduced which suggests that in these solvents sodium β-naphthoxide undergoes alcoholysis as well as ionisation.

The author is indebted to Mr. G. Rudd Thompson for facilities for this work, to Dr. J. C. Crocker for his continued interest, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the expense.

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LIV.—*The Introduction of the Chloromethyl Group into the Aromatic Nucleus.*

By Henry Stephen, Wallace Frank Short, and Geoffrey Gladding.

Up to the present time, it does not appear that any systematic attempt has been made to prepare benzyl chloride and benzyl bromide and their derivatives by direct introduction of chloromethyl and bromomethyl groups, respectively, into the aromatic nucleus.

Grassi-Cristaldi and Maselli (*Gazzetta*, 1898, **28**, ii, 477) were the first to show that the product (which they called chloromethyl alcohol) obtained by the action of hydrogen chloride on paraformaldehyde reacted with benzene in presence of aluminium chloride to yield benzyl chloride and diphenylmethane. Under such conditions, however, traces only of benzyl chloride could have been formed, since it would react very readily with unchanged benzene in presence of aluminium chloride to form diphenylmethane.

In this paper is described the preparation of benzyl chloride and compounds related to it by the direct introduction of the chloromethyl group into an aromatic compound. The method consists of treating an aromatic compound in presence of a

dehydrating agent with the product obtained by the action of hydrogen chloride on paraformaldehyde or aqueous solutions of formaldehyde, which has been shown to consist of *s*-dichloromethyl ether (Tischtschenko, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 464; Lösekann, *Chem. Zeit.*, 1890, **14**, 1408; Litterscheid, *Annalen*, 1901, **316**, 157; Litterscheid and Thimme, *Annalen*, 1904, **334**, 1). If methyl alcohol is present in the commercial formaldehyde employed, a small amount of monochloromethyl ether will also be present (Henry, *Ber.*, 1893, **26**, 933).

Both these compounds yield chloromethyl derivatives when treated with aromatic compounds in the presence of a dehydrating agent, but there is an essential difference between the two cases, for whilst *s*-dichloromethyl ether reacts very readily with benzene in the presence of anhydrous zinc chloride to give benzyl chloride, monochloromethyl ether under similar conditions reacts slowly. If zinc chloride monohydrate is substituted for anhydrous zinc chloride in the latter case, the reaction takes place readily. A possible explanation of these facts is indicated by the following scheme:

(i) $(CH_2Cl)_2O + 2C_6H_6 = 2C_6H_5 \cdot CH_2Cl + H_2O$.
(ii) $CH_3 \cdot O \cdot CH_2Cl + H_2O - CH_3 \cdot OH + CH_2Cl \cdot OH$.
(iii) $2CH_2Cl \cdot OH - (CH_2Cl)_2O + H_2O$.

The formation of benzyl chloride is explained by (i), and the water produced in the reaction would thus be available to bring about the hydrolysis of monochloromethyl ether according to (ii), two molecules of the chloromethyl alcohol thus formed then uniting with elimination of water to produce *s*-dichloromethyl ether. The reactions indicated by (ii) and (iii) explain why the monohydrate of zinc chloride brought about a quicker reaction between benzene and monochloromethyl ether. Furthermore, it has been observed that when monochloromethyl ether (b. p. 59—61°) was treated with the monohydrate of zinc chloride at about 27° and the mixture vigorously agitated, the product was *s*-dichloromethyl ether (b. p. 105—106°). The temperature of 27° is that at which the monohydrate deposits anhydrous zinc chloride.

The formation of a chloromethyl aromatic compound is usually accompanied by the production of a diphenylmethane derivative, which is formed by the condensation of the chloromethyl compound with the original aromatic compound. The latter reaction depends on the kind of dehydrating agent employed, since those reactions in which zinc chloride was used only furnished small amounts of the diphenylmethane derivatives, whereas the use of sulphuric acid under similar conditions invariably caused the formation of larger quantities of those substances. In both instances, however, the

temperature is an important factor, because, as a rule, diphenylmethane derivatives are formed to some extent by heating a mixture of a chloromethyl compound with another aromatic compound; the conditions for this reaction are more favourable when substances such as sulphuric acid, metallic oxides, or even traces of metals like iron, zinc, and mercury are present. Diphenylmethane was formed, for example, by treating benzyl chloride with benzene and concentrated sulphuric acid, and in absence of benzene a substance of complex nature was formed by the reaction of benzyl chloride with itself. Hydrogen chloride was copiously evolved in both reactions. The above statements hold true for other chloromethyl compounds, and as a result of preliminary investigations it was considered advisable to perform the reactions at temperatures not exceeding 35° in most cases, as otherwise the yield of chloromethyl derivative is diminished and the amount of diphenylmethane derivative increased.

For convenience, the various cases investigated which have led to the formation of chloromethyl or bromomethyl derivatives have been tabulated, as follows:

Compound investigated.	Compounds prepared.
Benzene	Benzyl chloride, $\omega\omega'$-dichloro-*p*-xylene, benzyl bromide.
Toluene	ω-Chloro-*p*-xylene, ω-bromo-*p*-xylene.
Xylene (commercial)	ω (1)-Chloro-ψ-cumene.
Benzyl chloride	$\omega\omega'$-Dichloro-*p*-xylene.
Benzyl bromide	$\omega\omega'$-Dibromo-*p*-xylene.
Chlorobenzene	*p*-Chlorobenzyl chloride, *p*-chlorobenzyl bromide.
Bromobenzene	*p*-Bromobenzyl chloride, *p*-bromobenzyl bromide.
o-Chlorotoluene	2-ω (4)-Dichloro-*p*-xylene.
Nitrobenzene	*m*-Nitrobenzyl chloride.
o-Nitrotoluene	ω (4)-Chloro-2-nitro-*p*-xylene.
p-Nitrotoluene	ω (2)-Chloro-4-nitro-*o*-xylene.

In addition to the above, other substances have also been investigated, but the results obtained were either unsuccessful or no reaction was observed. Diphenyl, for example, gave $\omega\omega'$-dichloro-*p*-ditolyl, but this we were unable to obtain in a pure condition, the evidence for its formation depending on the fact that the crude product gave diphenyl-4:4'-dicarboxylic acid on oxidation. Naphthalene, when mixed with dichloromethyl ether and allowed to remain at the ordinary temperature for two days, gives a product which resembles that described by Wheeler and Jackson (*J. Amer. Chem. Soc.*, 1902, **24**, 752) from formaldehyde and naphthalene. It possesses remarkable stability towards reagents such as potassium permanganate and chromic acid, and is only slightly attacked by fusion with a mixture of potassium hydroxide and potassium chlorate. Anthracene and anthraquinone were

recovered unchanged from the reaction mixtures, as was also the case with *m*-dinitrobenzene and *s*-trinitrotoluene respectively.

Phenol gave the well-known "bakelite" product, whereas from anisole good yields of *pp'*-dimethoxydiphenylmethane were obtained. The latter substance is also readily obtained by warming anisyl chloride (prepared by treating anisyl alcohol with phosphorus pentachloride in dry ether) with anisole.

In the cases of bases such as aniline, *o*-, *m*-, and *p*-toluidines, the so-called anhydro-bases were obtained. Dimethyl and diethyl aniline readily yield tetramethyl- and tetraethyl-diaminodiphenylmethane respectively. No reaction was observed with *o*- and *p*-chloronitrobenzene, *p*-dichlorobenzene, or *p*-chlorotoluene.

The introduction of a chloro- or bromo-methyl group into monosubstituted benzenoid compounds, such as toluene or chlorobenzene, appears to take place exclusively in the para-position. No evidence was found of the presence of the corresponding ortho-derivatives in the products. Benzyl chloride similarly gave only $\omega\omega'$-dichloro-*p*-xylene.

The presence of a nitro-group directs a chloromethyl group into the meta-position.

Experimental.

The Action of Hydrogen Chloride on Formaldehyde, Paraformaldehyde, and Hexamethylenetetramine.

Formaldehyde.—The apparatus consisted of a tower packed with glass beads, and the lower end was inserted in one neck of a Woulfe's bottle, which was provided with an outlet tap at the bottom. At the top of the tower, a suitable condensing arrangement was attached. Formaldehyde solution (40 per cent.) was allowed to percolate slowly down the tower, and at the same time a rapid stream of hydrogen chloride was passed upwards through the other inlet of the Woulfe's bottle. The reaction soon became evident from the fact that the tower was warm after the first two or three minutes. As the liquid collected in the receiver, the formation of oil was observed almost at once, and as the quantity of liquid increased, the oil was seen floating on the acid layer. The oil sinks only after saturation with hydrogen chloride, and the above method therefore has the advantage of yielding oil containing less hydrogen chloride than is the case in Lösekann's method.

It is important to note that when hydrogen chloride was passed into formaldehyde solution (40 per cent.), and the latter cooled

during the experiment by immersion in cold water, paraformaldehyde separated from the solution. It is difficult to convert paraformaldehyde into oil by this method when formed in such circumstances.

For satisfactory yields of oil, it is essential, therefore, that the heat produced during the reaction between formaldehyde solution and hydrogen chloride should be allowed to develop; the temperature seldom exceeded 60°, and in the tower experiment described above there was no appreciable loss of formaldehyde due to rise in temperature.

Paraformaldehyde.—Thirty grams (1 mol.) of paraformaldehyde were suspended in 40 grams of concentrated sulphuric acid (D 1·73), the mixture was cooled to 0°, and 175 grams (1·5 mols.) of chlorosulphonic acid were slowly added. The reaction is easily controlled by carefully adjusting the flow of chlorosulphonic acid, and the temperature should not be allowed to rise above 10°, otherwise the reaction becomes very violent and much paraformaldehyde is lost as vapour. The yield of *s*-dichloromethyl ether is 95 per cent. of the theoretical (compare *J. Soc. Chem. Ind.*, 1919, **38**, 468R).

Hexamethylenetetramine.—Twenty grams of hexamethylenetetramine were dissolved in 150 c.c. of concentrated hydrochloric acid, the solution was cooled in ice, and a rapid stream of hydrogen chloride was introduced. After ten minutes, a layer of oil was formed on the surface of the liquid, with simultaneous deposition of ammonium chloride. The oil was separated and purified, when it distilled at 105°, and only a small residue was left. The yield of *s*-dichloromethyl ether was about 50 per cent. of the theoretical.

In the experiments to be described later, the oil produced from 40 per cent. formaldehyde solution was employed, as being more economical and readily procurable. The presence of monochloromethyl ether does not affect the formation of chloromethyl derivatives when the oil is condensed with aromatic compounds, since it was found possible to prepare such derivatives from aromatic compounds and monochloromethyl ether. In the subsequent section dealing with the preparation of chloromethyl derivatives, the product from the action of hydrogen chloride on formaldehyde will be referred to as "crude oil." A rapid method for the preparation of small quantities of the "crude oil" consists in gradually adding sodium chloride to a suspension of paraformaldehyde in concentrated sulphuric acid, when the oil separates as an upper layer.

Properties of the Crude Oil.—On shaking the crude oil with sodium silicate, borax, or potassium carbonate, any excess of free hydrogen chloride is removed, the oil being slightly decomposed with the formation of paraformaldehyde; more decomposition

results if anhydrous sodium sulphate is used as a dehydrating agent.

The dry oil, from which excess of hydrogen chloride has been removed, is only slowly attacked by solid sodium or potassium hydroxides; the crude oil before drying is almost completely destroyed by such treatment.

Both the crude and treated oils are stable towards concentrated sulphuric acid, on which they float. Phosphoric oxide attacks the crude oil very vigorously, with the formation of paraformaldehyde; the oil treated as above is attacked only very slowly by this reagent.

The oil is volatile in a current of steam, about a half of it being destroyed in the process. This fact is of importance in connexion with the isolation of chloromethyl derivatives. These are obtained from the reaction mixtures by distillation in steam, and, in consequence, any unchanged oil is found mixed with such derivatives, and on purification of them by distillation, decomposition results. Unchanged oil may be easily removed by adding a little dilute potassium permanganate to the steam distillate until the colour of the solution is just pink; the oil is readily oxidised, and the odour of formaldehyde, usually present, disappears.

The Action of Hydrogen Bromide on Formaldehyde.

Thirty grams (1 mol.) of paraformaldehyde were suspended in 80 grams of sulphuric acid (D 1·84), the mixture was cooled in ice, and 155 grams (1·5 mols.) of finely powdered sodium bromide were slowly added with constant agitation. Only a small amount of bromine was evolved. The mixture was then warmed on the steam-bath for ten minutes, when the paraformaldehyde rapidly dissolved, and an oily layer of *s*-dibromomethyl ether appeared on the surface of the acid. On distillation of the crude product, about 80 grams of pure *s*-dibromomethyl ether were obtained (b. p. 154—155°). The properties of the oil are similar to those described for the corresponding chloro-compound.

The Preparation of Aromatic Chloromethyl Derivatives. Benzyl Chloride.

As the preparation of benzyl chloride is a typical example of the general mode of procedure, the following remarks are of general interest.

The yield of benzyl chloride is increased if the reaction is carried out at temperatures not exceeding 30°, the best results being obtained at the ordinary temperature. In most cases, it is neces-

sary to cool the reaction vessel with a rapid stream of cold water to avoid rise in temperature, the reaction mixture being well shaken by mechanical means or stirred by means of a rapid rotating Witt's stirrer.

In calculating the quantities of benzene and anhydrous zinc chloride to be used, so much of the latter was taken that if the reaction proceeded to completion, 2 molecules of water would be eliminated, forming zinc chloride dihydrate according to the equation

$$ZnCl_2 + 4C_6H_6 + 2(CH_2Cl)_2O = 4C_6H_5{\cdot}CH_2Cl + ZnCl_2,2H_2O.$$

It was found advantageous to use an excess of benzene in the condensation, otherwise unchanged *s*-dichloromethyl ether appeared in the distillate. A mixture of 108 grams of benzene and 68 grams of powdered anhydrous zinc chloride was shaken mechanically, and 79·5 grams of the crude oil added gradually, the temperature being kept below 25°. An immediate red coloration was observed, which became darker on further addition of the oil. When all the oil had been added, the shaking was continued for about an hour to complete the reaction. Ice-water was then added to the product, when the red colour disappeared, and the mixture was distilled in a current of steam.

Unchanged benzene distilled over rapidly, accompanied by the odour of formaldehyde, and at this stage the receiver was changed, as it was observed that the oil carried over in the distillate was heavier than water and possessed the characteristic odour of benzyl chloride as well as that of formaldehyde. When nearly the whole of the benzyl chloride had been removed, a white, crystalline mass was observed to solidify in the condenser. The distillation was then stopped, a pale brown oil remaining in the flask. This oily residue partly solidified on cooling, and was preserved, along with the white, crystalline mass mentioned above, for further investigation.

The aqueous suspension of the oil was treated with dilute potassium permanganate until the odour of formaldehyde had disappeared, the oil separated from water after settling, dried with anhydrous sodium sulphate, and distilled, 44 grams of benzyl chloride (b. p. 174°) being obtained.

Better yields were obtained using the entire crude product, that is, both the oil and the concentrated hydrochloric acid layers together with benzene, and sufficient anhydrous zinc chloride to convert the water present, and that produced during the reaction into the dihydrate, $ZnCl_2,2H_2O$.

The materials were added in the same order as in the previous

experiment, the temperature being kept below 10° and the mixture well shaken throughout.

Using 100 c.c. of formaldehyde (40 per cent.), 104 grams of benzene, and 140 grams of anhydrous zinc chloride, 57 grams of benzyl chloride were obtained. A brown-coloured residue also remained as before in the flask after distillation with steam.

In order to avoid the vigorous agitation required to emulsify the reaction mixture, on which the success of the operation largely depends, attempts were made to attain the same object by the use of finely divided kieselguhr. The results obtained were as follows, in each case 60 grams of crude oil being mixed with 100 grams of benzene and 68 grams of anhydrous zinc chloride.

Experiment.	Yield of benzyl chloride.	Time.
(I.) Kieselguhr ground with $ZnCl_2$	36 grams	1 hour.
(II.) Kieselguhr suspended in $ZnCl_2,H_2O$......	28 ,,	$\frac{3}{4}$,,
(III.) Finely powdered $ZnCl_2$	36 ,,	$2\frac{1}{2}$ hours
(IV.) $ZnCl_2,H_2O$..	28 ,,	$1\frac{3}{4}$,,

By comparison of the above experiments, it will be seen that agitation may be avoided by the use of kieselguhr, which also assists in diminishing the time required for the experiment without affecting the yield, and the possibility of formation of by-products was also eliminated. The yield of benzyl chloride is better when anhydrous zinc chloride is used rather than the monohydrated form, but the dehydrating properties of the latter in the presence of concentrated hydrochloric acid are better than the former, as is shown in the second experiment described above.

The dehydrating properties of the monohydrate of zinc chloride are of interest in connexion with the following experiment.

If pure monochloromethyl ether is condensed with benzene in the presence of zinc chloride in the manner above described, the following results are obtained, using 49 grams of benzene and 25 grams of monochloromethyl ether.

(i) Using anhydrous zinc chloride in sufficient quantity to form the monohydrate, 14·5 grams of benzyl chloride were obtained after five hours.

(ii) Using zinc chloride monohydrate in sufficient quantity to form the dihydrate, 14·5 grams of benzyl chloride were obtained after three-quarters of an hour.

These results are explained by the fact that hydrolysis of monochloromethyl ether must occur before the main condensation takes place, as mentioned in the introduction.

Thus, if no water is present in the zinc chloride, the reaction proceeds very slowly, since there is no tendency for the dehydration to take place until partial hydrolysis occurs.

In the case of the crude oil from formaldehyde, this contains much *s*-dichloromethyl ether, which may be condensed without hydrolysis to form benzyl chloride:

$$2C_6H_6 + (CH_2Cl)_2O = 2C_6H_6{\cdot}CH_2Cl + H_2O.$$

The change represented by this equation may be realised in practice by allowing a mixture of benzene and the crude oil to remain for several days. A small quantity of benzyl chloride is obtained, the formation of which is probably facilitated by the presence of hydrogen chloride dissolved in the crude oil.

In the reaction between benzene and *s*-dichloromethyl ether, water should be carefully excluded unless it has been previously saturated with hydrogen chloride, otherwise a considerable amount of hydrolysis of *s*-dichloromethyl ether takes place, according to the equation

$$(CH_2Cl)_2O + H_2O = 2HCl + 2CH_2O,$$

and this accounts for the poorer yields of benzyl chloride obtained if the monohydrate is used as dehydrating agent.

From Paraformaldehyde.—Thirty grams of paraformaldehyde and 127 grams of anhydrous zinc chloride were suspended in 100 grams of benzene, the mixture being cooled in ice and treated with dry hydrogen chloride for several hours. The product was then poured into water, and, on distillation in a current of steam and subsequent purification, 35 grams of benzyl chloride were obtained. A large residue remained in the flask after distillation with steam, the composition of which appeared to be of a very complex nature.

From Hexamethylenetetramine.—Forty grams of hexamethylenetetramine were mixed with 35 grams of powdered zinc chloride and suspended in 54 grams of benzene. Dry hydrogen chloride was passed into the mixture for eight hours, a red coloration being produced, which disappeared on pouring the mixture into water. Only a very small residue was left after distillation with steam, and the distillate, after purification, gave 5 grams of benzyl chloride.

An experiment was carried out with the object of combining the action of hydrogen chloride on formaldehyde with the subsequent one for the formation of benzyl chloride. Benzene (104 grams) was emulsified with formaldehyde solution (100 c.c. of 40 per cent.) by vigorous stirring, using a rapidly rotating Witt's stirrer, hydrogen chloride was passed into the emulsion, which was cooled in ice, and finely powdered zinc chloride (140 grams) added gradually during four hours. The yield of benzyl chloride was 23 grams, and much residue remained after distillation with steam. The disadvantage of this method is that the temperature is very difficult

to control, owing to the heat evolved during the action of hydrogen chloride on formaldehyde.

A further experiment, carried out without the use of zinc chloride, gave 10 grams of benzyl chloride, using the same quantities as before.

As stated previously, the use of sulphuric acid as a dehydrating agent instead of anhydrous zinc chloride in the above reactions gives poorer yields of benzyl chloride. The results obtained from a series of experiments indicate that the more concentrated the acid the smaller is the yield of benzyl chloride, and, in particular, sulphuric acid of concentration higher than 80 per cent. causes decomposition of the benzyl chloride formed during the reaction. On the addition of sulphuric acid (concentration varying from 80 per cent. and higher) to pure benzyl chloride, a copious evolution of hydrogen chloride took place, with the formation of a gum-like residue, which was insoluble in the usual organic solvents. Such a residue was the chief product obtained from the experiments, which also yielded only small amounts of benzyl chloride. In the case of sulphuric acid of concentration less than 80 per cent., the power of dehydration necessary for the reaction had been considerably diminished, and the operation was thus prolonged, a fact which militated against the success of the experiments.

*ωω′-Dichloro-*p*-xylene.*—The presence of this substance in the reaction mixture during the preparation of benzyl chloride has already been mentioned, and the amount was observed to increase when the reaction was carried out between 30° and 40°. A mixture of 72 grams of crude oil and 34 grams of finely powdered anhydrous zinc chloride was warmed at 35° for ten hours, during which time 39 grams of benzene were gradually added, the mixture being continually agitated. The latter became intensely red, the colour disappearing on pouring it into water at the end of the prescribed time. After the removal of the benzene and benzyl chloride in a current of steam, the residue was cooled, extracted with ether, the solution dried, and evaporated, when a semi-solid mass remained, which was distilled under diminished pressure, 22 grams of a white solid (b. p. 120°/20 mm., m. p. 97—99°) being obtained. It crystallised from ethyl alcohol in leaves melting at 100·5° (Lauth and Grimaux, *Zeitsch. f. Chem.*, 1867, **3**, 381, give 100°) (Found: Cl=40·28. Calc.: Cl=40·52 per cent.).

ωω′-Dichloro-*p*-xylene (10 grams) was also obtained by warming benzyl chloride (25 grams) and the crude oil with anhydrous zinc chloride at 30—35° for eighteen hours. After purification in the manner previously described, the substance melted at 100·5°. It

is readily soluble in cold chloroform or acetone and in hot ethyl or methyl alcohol, from which it crystallises, but sparingly soluble in ethyl acetate, benzyl chloride, ether, or glacial acetic acid. On warming with water at 80°, it is easily hydrolysed, the presence of free hydrochloric acid being detected in the aqueous portion. On oxidation, the substance gave terephthaldehyde (colourless needles, m. p. 116—117°, Hönig, *Monatsh.*, 1889, **9**, 1153) and terephthalic acid (m. p. 140°), the mononitro-derivative of the latter melting at 259°.

Benzyl Bromide.—This substance was prepared by treating benzene with the crude oil. The method of procedure was similar to that described in the case of benzyl chloride, and the same yields of benzyl bromide were obtained, the product distilling at 114°/15 mm.

ωω'-Dibromo-p-*xylene.*—This was isolated from the residue after removing benzyl bromide. After purification in the way already described for the corresponding chloro-compound, it crystallised from ethyl alcohol in glistening leaves melting at 144°, and on oxidation with potassium permanganate it yielded terephthalic acid.

ω-Chloro-p-*xylene.*—This was obtained (35 grams) from toluene (55 grams) by the methods previously described for benzyl chloride as a colourless liquid (b. p. 92—94°/20 mm., 192°/760 mm.) (Found: Cl = 23·9. Calc.: Cl = 24·3 per cent.). Its identity was established by the preparation from it of terephthalic acid, *p*-tolualdehyde (b. p. 102—105°/20 mm., 202°/758 mm.; oxime, m. p. 77—78°; *p*-nitrophenylhydrazone, m. p. 192°), and *p*-xylyl alcohol (m. p. 59°; acetate, b. p. 225—227°/758 mm., 121—123°/18 mm.).

ω-Bromo-p-*xylene.*—This was prepared by treating toluene with the crude bromo-oil and zinc chloride monohydrate. After purification, it was obtained as a heavy, colourless oil, which solidified after two distillations under diminished pressure (b. p. 109°/15 mm.), and the solid compound melted at 38° (Radziszewski and Wispek, *Ber.*, 1882, **15**, 1743, give 35·5°) (Found: Br = 43·09. Calc.: Br = 43·2 per cent.).

Di-p-*tolylmethane.*—This substance was isolated from the brown oil which remained after removing ω-chloro-*p*-xylene in a current of steam. The oil was dissolved in ether, the solution dried, evaporated, and the residue distilled, when a chief fraction consisting of a pale yellow oil passed over at 180°/13 mm. On redistillation under the ordinary pressure, the product was a colourless oil, boiling at 293°, which showed a faint blue fluorescence, and was insoluble in water, but readily soluble in the ordinary organic solvents. On cooling in a mixture of ice and salt, it solidified, and,

after draining the crystals and re-melting them, they showed a setting point of 22·5°. Ador and Rilliet (*Ber.*, 1879, **12**, 2302) give the melting point of di-*p*-tolylmethane as 23°, and Lavaux (*Compt. rend.*, 1911, **152**, 1400) gives 28° (Found: C=91·55; H=8·03. Calc.: C=91·82; H=8·16 per cent.).

A portion of the substance was nitrated by warming with nitric acid (D 1·42) on the water-bath at 60—70° until the oily layer had disappeared. On pouring into water, a white, crystalline substance separated, which was collected, washed with hot water, and then with sodium carbonate solution, in order to remove a small quantity of an acid formed by oxidation. The product was boiled with water, collected, and dried, and on crystallisation from acetic acid the first crop of crystals (plates) melted at 169—170°. A mixture of it with 3:3′-dinitrodi-*p*-tolylmethane (p. 526) showed no depression of the melting point. The filtrate deposited a further crop of crystals, which were twice recrystallised from acetic acid and then melted at 143—144°, and were identical with 3:3′-dinitro-4:4′-dimethylbenzophenone (p. 526). This substance is more readily soluble in acetic acid than the corresponding diphenylmethane derivative.

4:4′-*Dimethylbenzophenone*.—This was obtained by the oxidation of di-*p*-tolylmethane with chromic acid in acetic acid, the solution being kept cold. After an hour, the mixture was poured into much water, and the precipitate was collected, washed several times with sodium carbonate solution, and then crystallised from ethyl alcohol, from which the ketone separated in needles melting at 98° (Limpricht, *Annalen*, 1900, **312**, 92, gives 95°).

On fusion of the ketone with an excess of potassium hydroxide at 200°, the odour of toluene was observed, and the fused mass, after cooling and acidifying with hydrochloric acid, gave an acid which was crystallised from hot water, in which it was readily soluble, and melted at 177°. It was identified as *p*-toluic acid, and there was no evidence of the presence of *o*-toluic acid, which, however, is only sparingly soluble in hot water.

Prolonged action of chromic acid in acetic acid solution, or oxidation with potassium permanganate, converts di-*p*-tolylmethane into benzophenone-4:4′-dicarboxylic acid crystallising from acetic acid in needles, which sublime on heating (the silver salt gave Ag=44·4. Calc.: Ag=44·6 per cent.). The methyl ester melts at 224°, as stated by Limpricht (*loc. cit.*). Fusion of the acid with potassium hydroxide yielded a mixture of terephthalic and benzoic acids, which was easily separated, since the former is only very sparingly soluble in hot water, and the two constituents were identified in the usual way.

ω(1)-*Chloro-ψ-cumene* ($CH_2Cl:Me:Me = 1:3:4$).—It was not possible to study the reactions of the three xylenes individually, as these were not available. The above substance, however, was isolated from the product obtained by treating ordinary xylene with the crude oil, according to the method described in the case of toluene. It distils at 215—216° under the ordinary pressure (105°/15 mm.) (Curtius and Mayer, *J. pr. Chem.*, 1912, [ii], **85**, 143, give 103—104°/19 mm.), and possesses an odour resembling that of benzyl chloride (Found: Cl = 22·5. Calc.: Cl = 22·98 per cent.).

On reduction with red phosphorus and hydriodic acid, it gave ψ-cumene (b. p. 168—169°), the trinitro-derivative of which melted at 185°.

On converting into the aldehyde in the usual way, and subsequent oxidation of the latter, 2:4-dimethylbenzoic acid was obtained (m. p. 125°) (silver salt, found: Ag = 41·87. Calc.: Ag = 42·02 per cent.).

p-*Chlorobenzyl Chloride*.—This substance is readily prepared from chlorobenzene and the crude oil by any of the methods previously described. Good results were obtained by using zinc chloride monohydrate as dehydrating agent and carrying out the experiment at 65°. Employing 97 per cent. sulphuric acid at 25°, 50 per cent. of the chlorobenzene was converted into *p*-chlorobenzyl chloride, but higher temperatures favour the formation of 4:4′-dichlorodiphenylmethane; the yield of the latter is nearly theoretical at about 40°. *p*-Chlorobenzyl chloride was also obtained by treating chlorobenzene with monochloromethyl ether in the presence of dehydrating agents. It melted at 29° and boiled at 117°/20 mm. and 214°/758 mm. (Found: Cl = 44·48. Calc.: Cl = 44·1 per cent.). In order further to characterise this substance, *p*-chlorobenzoic acid (m. p. 236°), *p*-chlorobenzaldehyde (m. p. 46—47°), and *p*-chlorobenzyl alcohol (m. p. 70—71°) were prepared from it.

4:4′-*Dichlorodiphenylmethane*.—This substance was isolated from the residue after removing *p*-chlorobenzyl chloride in a current of steam. The brown oil was separated from the aqueous layer, dried, and distilled, when 4:4′-dichlorodiphenylmethane passed over as a colourless oil at 208—210°/15 mm., which solidified to a mass of white needles, and after crystallisation from methyl alcohol melted at 55°; this is identical with the value given by Montagne (*Rec. trav. chim.*, 1907, **25**, 390).

The compound was also obtained by treating *p*-chlorobenzyl chloride with chlorobenzene and sulphuric acid.

Five grams (1 mol.) of *p*-chlorobenzyl chloride were melted with 3·5 grams (1 mol.) of chlorobenzene, and, after cooling, the mix-

ture was treated with four times its weight of 97 per cent. sulphuric acid. It was then well shaken until emulsified and hydrogen chloride was evolved. The reaction was moderated by cooling in water, and the mixture was allowed to remain overnight. On passing a current of steam through the semi-solid mass after treatment with water, small amounts of unchanged chlorobenzene and *p*-chlorobenzyl chloride passed over, and 5 grams of 4:4′-dichlorodiphenylmethane were obtained from the residue by the method of purification described above.

4:4′-*Dichlorobenzophenone.*—This was obtained by treating 4 grams (1 mol.) of 4:4′-dichlorodiphenylmethane dissolved in 20 grams of glacial acetic acid with 4 grams (1 mol.) of chromic acid. The temperature of the solution rapidly rose, and it was necessary to cool the mixture in order to control the vigorous action which took place. After an hour, the dark green solution was poured into 250 c.c. of water, when glistening plates separated which, after crystallisation from ethyl alcohol, melted at 145°. The oxime melted at 136° (Dittrich, *Annalen*, 1891, **264**, 174, gives 135°). On fusing 4:4′-dichlorobenzophenone with potassium hydroxide, the odour of chlorobenzene was observed, and *p*-chlorobenzoic acid (m. p. 236°) was isolated.

4:4′-*Dichloro*-3:3′-*dinitrodiphenylmethane.*—Three grams of 4:4′-dichlorodiphenylmethane were dissolved in 20 c.c. of nitric acid (D 1·42) by warming on the water-bath, and the heating was continued for one hour. On pouring into water, a white, crystalline solid was deposited, which was collected, washed with hot water, dried, and crystallised twice from acetic acid, when it melted at 196°. The filtrate from the first crystallisation, on keeping overnight, deposited small, white needles, which melted at 132°, and there was no change in melting point when the substance was mixed with 4:4′-dichloro-3:3′-dinitrobenzophenone, prepared by nitrating 4:4′-dichlorobenzophenone.

The compound melting at 196° was analysed:

0·1205 gave 0·1049 AgCl. Cl=21·53.

$C_{13}H_8O_4N_2Cl_2$ requires Cl=21·71 per cent.

In order to determine the positions of the nitro-groups, the substance was oxidised with chromic acid in acetic acid solution in the usual way. The product crystallised from ethyl alcohol in small, hard needles melting at 132°, and consisted of 4:4′-dichloro-3:3′-dinitrobenzophenone.

The usual methods of carrying out the reactions described in the foregoing experiments have been applied to the preparation of the following compounds.

p-*Bromobenzyl Chloride.*—This was obtained from bromobenzene

and the crude oil in the presence of zinc chloride monohydrate. Forty-five per cent. of the bromobenzene was converted into *p*-bromobenzyl chloride, which, after purification, melted at 40° (Errera, *Gazzetta*, 1898, **18**, 239, gives 38—39°). Oxidation with potassium permanganate gave *p*-bromobenzoic acid (m. p. 251°).

4:4′-Dibromodiphenylmethane (m. p. 64°) was also isolated from the above reaction.

p-*Chlorobenzyl bromide*, prepared from chlorobenzene and the corresponding bromo-oil, crystallises from ethyl alcohol in needles melting at 48° (Jackson and Field, *Ber.*, 1878, **11**, 905, give 48·5°). Oxidation with potassium permanganate yielded *p*-chlorobenzoic acid.

p-*Bromobenzyl bromide*, prepared from bromobenzene and the bromo-oil, crystallised from methyl alcohol in needles melting at 60—61°. Oxidation converted it into *p*-bromobenzoic acid.

2-ω(4)-*Dichloro*-p-*xylene* ($CH_3:Cl:CH_2Cl = 1:2:4$).—This was prepared from *o*-chlorotoluene and the crude oil by treatment with zinc chloride monohydrate, the mixture being allowed to remain for twenty-four hours. After purification, it was obtained as a colourless oil boiling at 124°/20 mm.

Found: Cl=40·39.

$C_8H_8Cl_2$ requires Cl=40·52 per cent.

On oxidation with potassium permanganate, an acid was obtained, the ethyl ester of which (b. p. 149°) gave, on hydrolysis, 2-chloro-*p*-toluic acid (m. p. 195—197°) (Found: Cl=20·44. Calc.: Cl=20·8 per cent.). Gentle fusion of this acid with potassium hydroxide furnished 2-hydroxy-*p*-toluic acid (m. p. 204—205°).

m-*Nitrobenzyl Chloride*.—Many experiments were carried out with the object of preparing *m*-nitrobenzyl chloride from nitrobenzene and the crude oil, but only a small amount of the substance was isolated from any single experiment.

The best result was obtained by treating 63 grams of nitrobenzene with 80 c.c. of sulphuric acid (D 1·84) to which were added 10 c.c. of fuming sulphuric acid containing 10 per cent. of sulphur trioxide, adding gradually 45 c.c. of the crude oil, and maintaining the mixture at 50° for three days. The dark olive-green liquid was poured into four times its volumes of water and distilled in a current of steam; 56 grams of nitrobenzene were recovered, and 3 grams of a white substance solidified in the cool part of the condenser. A small amount of a dark brown solid was left in the flask.

The white solid was found to consist of *m*-nitrobenzyl chloride, which crystallised from ethyl alcohol in glistening plates melting

at 44·5°. It was converted by oxidation with potassium permanganate into *m*-nitrobenzoic acid (m. p. 139—140°), the methyl ester of which melted at 77·5°.

m-Nitrobenzyl chloride was also obtained by treating nitrobenzene and monochloromethyl ether in molecular proportions with aluminium chloride. The yield, however, is poor, and 3:3′-dinitrodiphenylmethane is the chief product.

ω(4)-*Chloro-2-nitro-*p*-xylene* ($CH_3:NO_2:CH_2Cl = 1:2:4$).—The action of sulphuric acid containing 10 per cent. of sulphur trioxide on mixtures of *o*-nitrotoluene and the crude oil resulted in the formation of small quantities of this compound. The following method, however, was found to give a satisfactory result.

Twenty grams of the crude oil were mixed with 20 grams of *o*-nitrotoluene, and to the clear solution 25 grams of finely powdered aluminium chloride were added during the course of two hours. The solution became darker, and heat was evolved. After remaining overnight, water was added and the mixture distilled in a current of steam, when a mixture of ω(4)-chloro-2-nitro-*p*-xylene and *o*-nitrotoluene passed over, leaving a brown oil in the flask. The mixture was separated by distilling off the *o*-nitrotoluene under diminished pressure.

ω(4)-*Chloro-2-nitro-*p*-xylene* was also obtained by treating a mixture of *o*-nitrotoluene and chloromethyl ether in molecular proportions with a little more than the theoretical quantity of aluminium chloride, and subsequently purifying by the method already described. There was no unchanged *o*-nitrotoluene, but a considerable amount of the brown oil, mentioned above, remained after distillation with steam.

The substance, after crystallisation from methyl alcohol, melts at 45°. It has a violent action on the skin, and the vapour attacks the eyes and nose. It is readily soluble in benzene, chloroform, acetone, or ethyl alcohol.

Found: Cl = 19·07.

$C_8H_8O_2NCl$ requires Cl = 19·11 per cent.

The position of the chloromethyl group was determined (i) by converting a portion of the material into 2-nitroterephthalic acid by oxidation with potassium permanganate; (ii) reduction with tin and hydrochloric acid, by which treatment the chlorine in the side-chain was replaced by hydrogen and the nitro-group reduced in the usual way, *p*-xylidine (b. p. 218°) being isolated from the mixture. The platinichloride was analysed, and the hydrochloride, acetyl and benzoyl derivatives melted at the same temperatures as are recorded in the literature.

3:3′-*Dinitrodi-*p*-tolylmethane*.—The brown oil mentioned in the

above preparation solidified on cooling in ice, was ground with a little ethyl alcohol, and the latter decanted, the operation being repeated several times in order to remove traces of the chloromethyl compound. It crystallised from acetic acid in thin, glistening plates melting at 170°. It is only sparingly soluble in hot ethyl or methyl alcohol, but very readily soluble in cold acetone. A mixture of this substance with the product obtained by treating *o*-nitrotoluene with formaldehyde solution and sulphuric acid (D.R.-P. 67001), which has been shown (Fischer and Gross, *J. pr. Chem.*, 1910, [ii], **82**, 231) to be 3:3′-dinitrodi-*p*-tolylmethane, melted at 170°.

3:3′-*Dinitro*-4:4′-*dimethylbenzophenone*.—This was obtained by oxidising the preceding compound with chromic acid in acetic acid solution at the ordinary temperature. The ketone was washed with dilute sodium carbonate solution, and it crystallised from acetic acid in yellow needles melting at 144°.

On fusion with potassium hydroxide, it undergoes fission at the carbonyl group, yielding 2-nitro-*p*-toluic acid and *o*-nitrotoluene, which were conveniently isolated as the corresponding oxidation products, nitroterephthalic acid and *o*-nitrobenzoic acid respectively. The corresponding 3:3′-diamino-compound and its diacetyl derivative melted at 172° and 196° respectively, as stated by Lange and Zufall (*Annalen*, 1892, **271**, 6).

ω(2)-*Chloro*-4-*nitro*-o-*xylene* ($CH_3:CH_2Cl:NO_2=1:2:4$).—The most satisfactory method of preparing this substance consisted in treating a mixture of 10 grams of *p*-nitrotoluene and 20 grams of crude oil with 50 grams of fuming sulphuric acid containing 20 per cent. of sulphur trioxide. After remaining overnight, the mixture was treated in the usual way, and ω(2)-chloro-4-nitro-*o*-xylene was finally obtained from methyl-alcoholic solution in needles melting at 50°.

The same substance may be prepared by using any of the methods described for the preparation of ω(4)-chloro-2-nitro-*p*-xylene, although the yields are not correspondingly as good.

Found: Cl=18·99.

$C_8H_8O_2NCl$ requires Cl=19·11 per cent.

ω(2)-*Chloro*-4-*nitro*-o-*xylene* is readily soluble in ethyl alcohol, benzene, or ether, but sparingly so in acetone or light petroleum, and its physiological action is similar to that of ω(4)-chloro-2-nitro-*p*-xylene. On reduction with tin and hydrochloric acid, it gave *o*-4-xylidine (m. p. 49°), which was identified by means of its acetyl derivative (m. p. 99°) and analysis of the platinichloride (Found: Pt=29·88. Calc.: Pt=29·93 per cent.).

On oxidation with potassium permanganate, ω(2)-chloro-4-nitro-

o-xylene is converted into 4-nitrophthalic acid (m. p. 159°), from which 4-nitrophthalanil (m. p. 192°) was prepared.

5:5′-Dinitrodi-o-tolylmethane was also isolated in the above reaction. It melted at 153° (Weil, *Ber.*, 1894, **27**, 3314), the corresponding 5:5′-diamino-compound at 99°, and the diacetyl derivative of the latter at 269°.

5:5′-*Dinitrobenzophenone*-2:2′-*dicarboxylic Acid*.—This compound was readily obtained by oxidising the corresponding diphenylmethane derivative with chromic acid in acetic acid solution, and subsequently treating the crude benzophenone derivative (which has not yet been isolated in a pure condition) with potassium permanganate. It crystallised from ethyl alcohol in well-defined needles, which did not melt at 300°:

0·2620 gave 0·4796 CO_2 and 0·0568 H_2O. C=49·92; H=2·43.

$C_{15}H_8O_9N_2$ requires C=50·01; H=2·34 per cent.

On fusion with potassium hydroxide, 4-nitrophthalic acid and p-nitrobenzoic acid were obtained.

In concluding, we desire to express our thanks to Professor Lapworth and Dr. J. E. Myers for the kind interest they have taken in the research.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY, MANCHESTER. [*Received, March 6th*, 1920.]

LV.—*A New Hydrogen Sulphide Generator.*

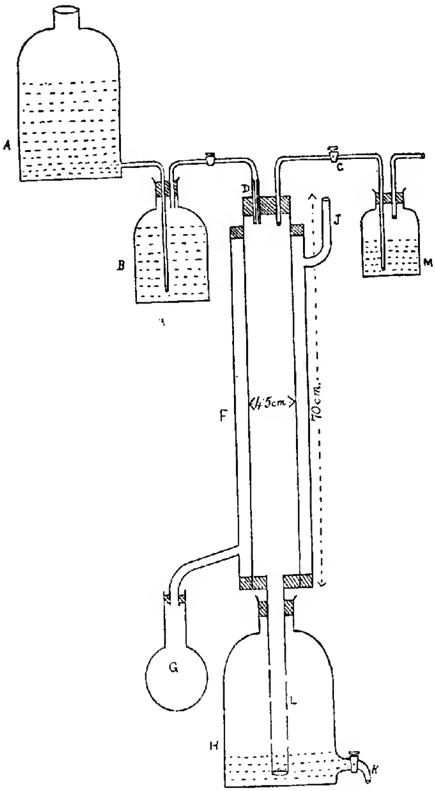
By BERTRAM DILLON STEELE and HENRY GEORGE DENHAM.

THE chief defects common to the usual laboratory forms of hydrogen sulphide generators are to be traced to the comparative slowness of the reaction between acid and sulphide, especially when the concentration of the acid has reached a low value. In consequence of this, a very large apparatus is necessary if it is desired to supply each member of a class with a constant supply of gas, and in order to attain this there is, in general, a great wastage of partly spent acid. In the apparatus herein described, an endeavour has been made to obtain (1) a rapid evolution of gas, and (2) complete neutralisation of the acid.

Preliminary experiments on the effect of temperature on the velocity of the reaction between iron sulphide and hydrochloric acid were carried out in 1911 by Mr. I. Rosenblum at the sugges-

tion of one of the authors, and it was soon established that the two desired objects could be readily attained by bringing about the reaction in the neighbourhood of 100°. The following apparatus was then designed:

A is the acid-holder containing about 15 litres, *B* a smaller



reservoir to retain hydrogen sulphide generated after the tap *C* is turned off, *D* a piece of capillary tubing, 3 cm. long and of 1 mm. bore, inserted to prevent a too rapid outrush of acid when the taps are opened, *F* represents a steam-jacket either of glass or of galvanised iron, *M* a wash-bottle, *H* a reservoir, of 25 litres capacity, to receive the spent acid, and *k* a tap through which the spent

acid may be readily removed. As a matter of convenience, it is advisable to have *H* sufficiently large to hold the maximum amount of acid required per demonstration. In order to facilitate the displacement of air from the vessel *H* by the incoming spent liquor, the tube *L* has a number of holes blown in it. The steam may be supplied from a 500 c.c. flask, *G*, and experience has shown that with a short air-condenser attached to *J* there is practically complete condensation of the escaping steam, so that little or no attention is required.

Mode of Operation.—The apparatus, *F*, is packed with lumps of iron sulphide, and the acid-holders are filled with commercial hydrochloric acid diluted with an equal volume of water. On opening the tap *C*, acid begins to drip on the sulphide, and, provided steam has been passed through the jacket for a sufficiently long period to ensure thorough heating of the sulphide, each incoming drop of acid reacts with almost explosive violence, and long before the acid has percolated through the heated column it is completely neutralised. In fact, a few pieces of iron sulphide placed in the receiver *H* were found to be unacted on after the apparatus had been in constant use for seven months. After generation, the gas passes through the tap *C* and the wash-bottle *M* before distribution to the students' benches. On turning off either the tap *C* or the bench taps, the gas generated by the last few drops of acid passes back into the holder *B* and forces acid into the upper vessel *A*.

General Remarks.—Hydrochloric acid (1 : 1) has been found to be more suitable than sulphuric acid, owing to the great tendency of ferrous sulphate to crystallise out as the spent liquor passes from the heated generator into the receiver, thereby causing a block.

The apparatus of the dimensions indicated in the figure is sufficiently large to supply hydrogen sulphide to the bench of every student in a class of fifty-four, and will stand all demands made on it when this class is engaged exclusively on the analysis of mixtures containing at least four bases from Groups II*A* and II*B*, even to the extent of enabling them to prepare their own ammonium sulphide. As an example of the economy of the apparatus, a series of tests showed that the average consumption of concentrated hydrochloric acid per demonstration of two hours by each student engaged as above in Group II analysis amounted to 14 c.c., which was equivalent to 2300 c.c. of hydrogen sulphide at normal pressure and the ordinary temperature.

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LVI.—*Direct Experimental Determination of the Concentration of Potassium and Sodium Ions in Soap Solutions and Gels.*

By Cyril Sebastian Salmon.

In a series of papers from this laboratory (McBain, *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **12**, 256; *J. Soc. Chem. Ind.*, 1918, **37**, 249T; McBain and Martin, T., 1914, **105**, 957; McBain and Salmon, *Proc. Roy. Soc.*, 1920, [*A*], **97**, 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426; McBain, Laing, and Titley, T., 1919, **115**, 1279), a theory of soap solutions has been developed which quantitatively correlates their high conductivity, moderate osmotic activity, and colloidal properties. Soaps are conceived as a type of a large class of substances, defined as colloidal electrolytes, which owe their properties to the presence of a heavily hydrated, highly charged, excellently conducting ionic micelle.

Hitherto, in the few cases where colloidal ions were envisaged, kataphoresis was confounded with conductivity, and to such colloidal ions was then ascribed a low mobility, such as that to be expected from a complex ion, or it is a well-known and striking fact that the kataphoresis of colloidal particles, and even of coarse suspensions, is in general almost comparable in velocity with the movement of a slow ion. Moreover, it was only in the few cases referred to that kataphoresis was interpreted as conductivity.

The carefully substantiated data for soap solutions obtained by several independent and corroboratory methods force us to ascribe to the ionic micelle an equivalent conductivity which is even greater than the sum total of the conductivities of the ions from which it is derived. This is explained on mechanical grounds, making use of the principle of Stokes's law by conceiving the ionic micelle as an aggregation of fatty ions, such as palmitate ions, which have retained their electrical charges. The ionic micelle must include also, and is probably stabilised by, a large amount of neutral colloid and of hydrate water.

It is clear that the ionic micelle must possess high electrical mobility, but very low mechanical mobility. Under the influence of electrical forces, the mobility of the micelle is magnified in direct proportion to the number of ionic charges which it comprises, whereas for purposes of diffusion the driving force is only that of an individual ion.

The object of the present investigation was twofold: first, t

test as directly as possible the quantitative data already deduced by our theory by a further independent method, and, secondly, to demonstrate this distinction between electrical and mechanical mobility. The method employed was that of electromotive force, using potassium and sodium electrodes. The results are as good a quantitative confirmation as could be expected. The solutions actually studied were potassium laurate at room temperature, since it is the highest soap which gives a clear solution at the ordinary temperature and yet shows all the characteristics of a higher saturated soap, potassium and sodium oleates at the ordinary temperature, and sodium palmitate at 90°, since it has been in other respects the most carefully investigated soap.

EXPERIMENTAL.

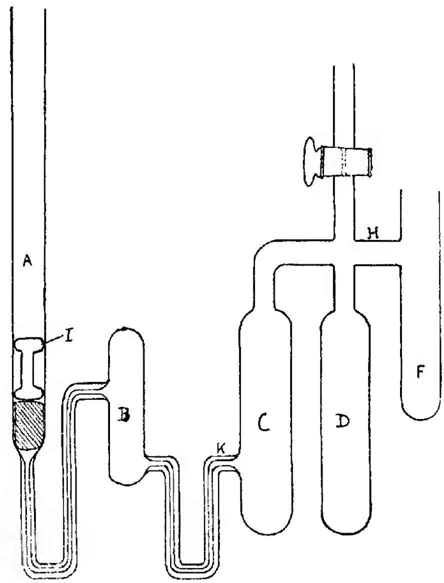
The fatty acids used and the precautions taken in the preparation of the soap solutions were similar to those described in previous communications.

The amalgam for these experiments was prepared in a pure state by filtering potassium free from oxide through a capillary tube in an inert atmosphere, and distilling mercury into the pure metal so obtained. The apparatus used for the purpose (Fig. 1) is a modified form of that employed by Lewis and Krauss (*J. Amer. Chem. Soc.*, 1910, **32**, 1959; Lewis and Keyes, *ibid.*, 1912, **34**, 119), who were the first to measure the potentials of both sodium and potassium electrodes. The bulb *D* contains mercury previously purified by washing with mercurous nitrate and distillation in a current of air. The apparatus is washed out with dry ammonia gas, and, while the gas is still streaming through, a clean bulb of potassium is introduced into the tube *A* and another into *F*. *A* and *F* are then sealed, and the apparatus is exhausted. The object of the potassium at *F* is to remove all remaining oxygen or water vapour. This is ensured by melting the metal and constantly renewing the surface by tapping the tube until a surface is obtained which remains untarnished. *F* is then removed by sealing at *H*. The apparatus is heated to 120°, the potassium in *A* melts, and is forced by the glass weight *I* through the capillary tube into the bulb *B*, which acts as a trap for any oxide that may have been carried along with the metal. Tubes *A* and *B* are removed by sealing at *K*, and the mercury in *D* is distilled into *C* by raising the temperature to 250°. The resulting amalgam is thoroughly mixed by shaking, and may be kept unchanged for long periods.

Fig. 2 shows the type of electrode used. *A* is a reservoir for

the amalgam, and is connected to the electrode chamber I by a two-way stopcock and capillary tube, B. (The two-way cock serves to facilitate cleaning the capillary between measurements.) Electrical contact is made by sealing a platinum wire through the capillary tube at E. The reservoir is filled by sealing the electrode vessel at C to the apparatus in which the amalgam is prepared, washing out with ammonia gas, exhausting, and then opening the stopcock of the amalgam vessel. After filling, the electrode vessel

FIG. 1.



Apparatus for the preparation of clean potassium amalgam.

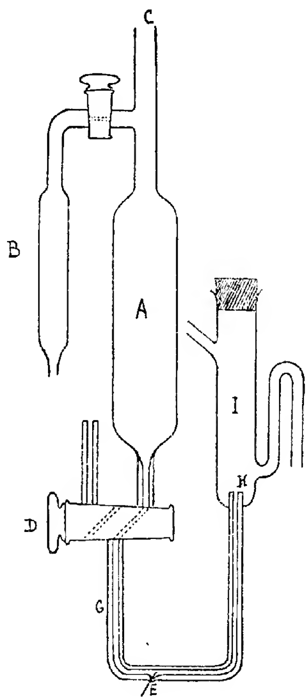
is sealed off at C. The calcium chloride tube serves to admit dry ammonia gas to displace the amalgam as it is used.

The solution to be investigated is placed in the electrode chamber, I, and amalgam admitted to the capillary tube until a small drop forms at H. At first this reacts slightly with the water, and the surface becomes contaminated with hydrogen, but it was found that by renewing the drop once or twice, surfaces could be obtained which remained clear for from ten to twenty

minutes. During this period the electromotive force remains constant, but then commences to fall off rapidly. On renewing the surface, however, the *E.M.F.* returns to its original value.

The *E.M.F.* was measured by the potentiometer method, using two carefully calibrated resistance boxes (both of 111,110 ohms

FIG. 2.



Electrode for potassium amalgam.

otal resistance) instead of a bridge wire. By keeping the total esistance in the two boxes 111,110 ohms and varying the ratio etween them, measurements could be made to within less than ne-tenth millivolt.

The electrode potentials were measured against the *N*-calomel lectrode, using 0·2*N*-potassium chloride as intermediate liquid in

most cases. The cell measured was then of the following type, the arrow showing the direction of the current in the cell:

$$\text{K amalgam} \mid N\text{-K laurate} \mid 0{\cdot}2N\text{-KCl} \mid N\text{-KCl,HgCl} \mid \text{Hg}.$$
$$\longrightarrow$$

(a) *Potassium Laurate at 25° as compared with Potassium Chloride.*

Table I gives the results obtained with three concentrations.

The values in columns in *A*, *B*, *C* represent three different series of measurements carried out with different specimens of amalgam and of potassium laurate, and against a different normal electrode. The agreement between these series is sufficiently good for our purpose, which is to ascertain the concentration of potassium ions in soap solutions by direct comparison with known solutions of potassium chloride.

TABLE I.

Electrode solution.	Middle liquid.	*E.M.F.* (Volts.) *A.*	*B.*	*C.*
N-K laurate	0·2*N*-KCl.	2·183	2·197	2·219
0·5*N*- „	„	2·196	—	2·233
0·2*N*- „	„	2·205	—	2·245
0·5*N*-KCl	„	2·159	2·176	2·196
0·2*N*- „	„	2·182	2·199	2·219

TABLE II.

Potassium Laurate with Different Concentrations of Potassium Chloride as Middle Liquid.

Electrode solution.	*E.M.F.* (Volts.) 0·2*N*-KCl.	0·05*N*-KCl.	0·01*N*-KCl.
N-K laurate	2·219	2·235	2·253
0·5*N*- „	2·233	2·241	2·263
0·2*N*- „	2·245	2·252	2·264

TABLE III.

Potassium Laurate with Different Concentrations of Sodium Chloride as Middle Liquid.

Middle liquid.	*E* calc.	*E* found.
0·2*N*-NaCl	2·244	2·241
0·05*N*- „	2·255	2·254
0·01*N*- „	2·268	2·268

(b) *Potassium Oleate at* 18°.

Potassium laurate had been chosen for investigation as being the highest member in the saturated fatty acid series which could be studied at the ordinary temperature. Potassium oleate, the salt of an unsaturated fatty acid of higher molecular weight, is more colloidal in its behaviour, and its colloidal properties persist in greater dilution than the laurate, whilst its solutions of moderate concentration are quite clear liquids. The highest concentration ($0{\cdot}6N$), which gave a clear solution, was therefore measured for comparison with potassium laurate. Determinations carried out with three different concentrations of potassium chloride as middle section are given in table IV.

TABLE IV.

	$0{\cdot}1N$-KCl.	$0{\cdot}05N$-KCl.	$0{\cdot}01N$-KCl.
$0{\cdot}6N$-K oleate......	2·239 volts.	2·245 volts.	2·276 volts.

(c) *Sodium Palmitate at* 90°.

The results obtained for potassium laurate and potassium oleate at the ordinary temperature confirm the hypothesis of an ionic micelle for these solutions, but since a great part of the existing data for soap solutions was obtained at 90°, it was considered desirable to obtain at least one measurement at that temperature with the sodium electrode. The experimental difficulty in working at this temperature lies in the fact that it is difficult to obtain an amalgam which will not react with water. It was found, however, that it was just possible to obtain measurements which, although not very accurate, are yet sufficiently trustworthy to obtain at least a quantitative measurement. A N-solution of sodium palmitate was selected for this measurement, since it is one of the most typical soap solutions and the most carefully investigated.

The amalgam was prepared in exactly the same way as potassium amalgam. In carrying out the experiment, two middle sections were used of the same concentration of potassium chloride, one at 90° and the other (communicating with the calomel electrode) at the ordinary temperature, thus keeping the temperature gradient in potassium chloride. Connexion between the soap and the potassium chloride was made by means of a fine capillary tube full of the latter. Table V contains the results for three different middle sections.

TABLE V.

	0·1N-KCl.	0·05N-KCl.	0·01N-KCl.
N-Na palmitate...	2·263 volts.	2·272 volts.	2·295 volts.

The electrode potentials of $N/2$- and $N/5$-sodium chloride were also measured with 0·1N-potassium chloride as middle section. They were found to be 2·237 and 2·261 volts respectively.

(d) *Sodium Oleate as Sol and as Gel at* 18°.

A 0·6N-solution of this soap was investigated, since it can be obtained at the ordinary temperature in three states, namely, as viscous sol, a clear, transparent gel, and white, opaque curd.

Measurements were carried out at 18° with the sol and gel by the method already described, but it was found impossible to obtain trustworthy results with the curd. Figures for the sol and gel are given in table VI.

TABLE VI.

Middle liquid.	Sol.	Gel.
$N/5$-NaCl	2·284	2·283
$N/10$-NaCl	2·295	2·293
$N/100$-NaCl	2·315	2·314

It will be seen from the above table that the concentration of the sodium ion is the same in the sol and gel. This will be discussed in another paper by Miss M. E. Laing. It is sufficient to say here that the calculated values of V_1, E, and C_1 (see below) are 1·0 mhos., 21 millivolts, and 0·11 normal. The *E.M.F.*, corrected for diffusion potential, thus becomes 2·263 volts; that of $N/5$-sodium chloride is 2·254. From these values we obtain a concentration of sodium ions of 0·11N, which agrees with that required by the data of McBain, Laing, and Titley. Moreover, it should be noticed that the diffusion potential is not affected by the gelation of the sodium oleate.

The Calculation of Diffusion Potential for the Case of an Electrolytic Colloid.

In the introduction above it was made clear that, except where an electrical field of force is the driving agent, it is the mechanical, and not the electrical, mobility of the ionic micelle that will be in evidence. The diffusion potential will therefore depend on the mechanical diffusion velocity of the ionic micelle, taken in con-

junction with that of the other ions present, for which, of course, mechanical and electrical diffusion velocity are identical.

Before calculating the concentration of potassium ion from the measurements given, it is therefore necessary to evaluate the liquid potential between such solutions as potassium laurate and potassium chloride. This is by no means negligible, since the rate of diffusion of the potassium ion is many times that of the laurate ion or micelle.

It was finally determined in the following manner. The Henderson formula for a liquid potential gives

$$E = \frac{RT}{V} \cdot \frac{C_1(U_1 - V_1) - C_2(U_2 - V_2)}{C_1(U_1 + V_1) - C_2(U_2 + V_2)} \ln \frac{C_1(U_1 + V_1)}{C_2(U_2 + V_2)},$$

where, in the case under consideration, the concentration, C_1, and the mobilities, U_1 and V_1, refer to potassium laurate, and C_2, U_2, and V_2 to potassium chloride.

V_1 must be the effective diffusion velocity of the ionic micelle, together with that of any laurate ions present. It is not easy to calculate this resultant with any accuracy from previously available data, but if we consider the above equation, there are only three unknown quantities, C_1, the concentration of potassium ion in soap solutions, V_1, and E, the diffusion potential itself. It is only necessary to obtain three equations connecting these quantities in order to evaluate them. This can be done by using different concentrations of potassium chloride as middle section, data for which were given in table II. The values for C_1, E, and V_1, calculated from these figures, are shown in table VII.

TABLE VII.

Solution.	V_1 (mhos).	E (millivolts).	C_1 (normality).
N-K laurate	14	17	0·33
0·5N- „	18	13	0·16
0·2N- „	25	7	0·082

It is at once seen that V_1 increases with increasing dilution. This is in accordance with theory, since we know that the relative amount of soap present as crystalloid is greater in dilute solutions than in more concentrated ones. In other words, the more rapidly diffusing laurate ion is being displaced by the more slowly diffusing micelle,* and in the most dilute solution, V_1, approaches the mobility of the former.

* This is, of course, in the opposite direction to the effect of dilution on conductivity, where the displacement of the micelle by ion decreases the mobility.

The values of the diffusion potential are quite large and affect the concentration value of the potassium ion by comparison with the potassium chloride so much that it was considered necessary to test the applicability of the Henderson formula to the present case before accepting these results, especially in view of the fact that we are giving to V_1 a meaning different from that usually given to it. Measurements were therefore carried out, using sodium chloride as middle section. The results of these determinations were given in table III, where, under the column E calc., were given the *E.M.F.*'s of the cell calculated from the value of C_1 and V_1 obtained above. E found contains the experimentally determined values.

The agreement between the calculated and experimentally determined values is quite satisfactory, and we are therefore justified in accepting these values of the diffusion potential so determined as being trustworthy. It will be noted that the diffusibility, V_1, is by no means equal to zero, even for concentrated solutions where the ionic micelle has almost completely displaced the simple fatty ion. It is, indeed, quite a large fraction of the value 20·7, which one expects for a simple fatty ion containing from twelve to eighteen carbon atoms. The explanation is to be sought in the dissociation of soap and micelle that takes place when it diffuses into aqueous potassium chloride, which previously contained no soap. It is proposed to calculate these values later, when the equilibria in soap solutions containing admixtures of chlorides have been sufficiently investigated. It may be pointed out that the concentrations dealt with in the present paper are such that salting out does not occur at the boundaries of salt and soap solutions.

It is now possible to introduce the corrected diffusion potentials in the measurements which McBain and Martin carried out on the hydrogen potential of soap solutions. This affects chiefly the more concentrated solutions, and the result is a diminution in the concentration of the alkali formed on hydrolysis, which still further emphasises its negligible character in concentrated soap solutions. The corrected results will be included in another communication from this laboratory.

Discussion of Results.

I. *Potassium Laurate.* (a) *Concentration of the Potassium Ion.*

The concentration of the potassium ion has already been obtained in the solution of the Henderson formula, but it can be calculated in another manner by comparing the *E.M.F.*, corrected

for this diffusion potential, with that obtained for potassium chloride. These values are given in table VIII.

TABLE VIII.

Solution.	Corrected *E.M.F.*	Normality of $K^{\cdot}$.
N-K laurate	2·202	0·33
0·5*N*- „	2·218	0·17
0·2*N*- „	2·238	0·082
(0·2*N*-KCl)	(2·219)	(0·167)

The concentrations measured in this manner agree closely with those tabulated in table VII.

(b) *Comparison with Conductivity and Osmotic Data.*

McBain, Laing, and Titley (*loc. cit.*) have calculated the concentration of potassium ion in solutions of potassium laurate, from conductivity data, making the assumption that the laurate micelle has the same electrical mobility as the potassium ion. These values are included in table IX for comparison with those recorded above, together with the total concentration of crystalloid present calculated from osmotic data.

TABLE IX.

Solution.	Concentration of $K^{\cdot}$ by *E.M.F.*	Concentration of $K^{\cdot}$ by conductivity.	Concentration of crystalloid by osmotic data.
N-K-laurate	0·33*N*	0·36*N*	0·40*N*
0·5*N*- „	0·17*N*	0·176*N*	0·20*N*
0·2*N*- „	0·082*N*	0·065*N*	0·136*N*

The agreement between columns two and three is sufficiently close to afford confirmation of the existence of the ionic micelle and to justify the assumption made as to its mobility. For the most concentrated solutions, the conductivity value is higher than that calculated from electromotive force data. To bring these two values into agreement, it would be necessary to ascribe to the micelle a still greater mobility; but it is doubtful if we are justified in doing so, since, in general, conductivity and osmotic data do not closely agree.

In the lowest concentration the conductivity value is low, and the difference between it and the *E.M.F.* value is undoubtedly real. This is explained by the substitution of the laurate ion for the micelle, and consequent decrease in electrical mobility. In this solution, the concentration of colloid present as micelle is 0·038*N*, and of the laurate ion 0·044*N*. If we calculate an average

value for the combined mobility of the micelle and ion from th relation $V = \alpha Vm + (1-\alpha)V_2$, where α is the proportion of soap a micelle and $(1-\alpha)$ is the proportion as ion, and Vm and V_2 ar the respective mobilities of the micelle and ion, we obtain 40·9 a the combined mobility. Substituting this value in the conduc tivity calculation, we find $\alpha = \frac{41 \cdot 7}{105 \cdot 6}$. This gives the concentratio of potassium ion as $0 \cdot 078N$, which is in much closer agreement wit the electromotive force value.

In N-potassium laurate, the concentration of the total crystal loid is $0 \cdot 4N$, and that of the potassium ion 0·33, leaving only 0·0 for all other crystalloid, including undissociated potassium laurate laurate ion, and hydroxyl ion.

In $0 \cdot 2N$-potassium laurate, the concentration of crystalloid other than $K^{\cdot}$, is $0 \cdot 054N$, relatively a much greater quantity. Thi transition from colloid to crystalloid with increasing dilution i quite gradual and regular.

(c) *The composition of the Ionic Micelle.*

We are now in a position to calculate the approximate concen tration of all the constituents of potassium laurate solutions These are given in table X, all concentrations being expressed ir mols. per 1000 grams of water.

TABLE X.

Solution.	$K^{\cdot}$.	L'.	KL.	Micelle $(L')_n$.	Neutral colloid $(KL)_m$.
N-K-laurate	0·33	0·04	0·03	0·29	0·64
$0 \cdot 5N$- ,,	0·17	0·02	0·01	0·15	0·32
$0 \cdot 2N$- ,,	0·082	0·044	0·01	0·038	0·04

It is not yet possible to determine with certainty whether the formula of the micelle is $(L')_n(H_2O)_x$ or $(KL)_n(L')_m(H_2O)_x$. We consider it most probable that part of the neutral colloid is absorbed in the micelle. The formula, calculated on the assumption that the whole is taken up, would be $[(KL_{2 \cdot 2})(L')H_2O_x]_n$.

II. *Potassium Oleate.*

The values for V_1, E_1, and C_1, calculated from the data of table IV, are 12 mhos., 22 millivolts, and $0 \cdot 19N$ respectively. The corrected *E.M.F.* becomes 2·217, and comparing this value with the corresponding *E.M.F.* for $0 \cdot 2N$-potassium chloride, which is 2·219 volts, we obtain $0 \cdot 185N$ for the concentration of the potassium ion in $0 \cdot 6N$-potassium oleate.

The value of V_1 is considerably lower than that for the corresponding concentration of laurate; this would be expected, on account of the higher molecular weight of oleic acid.

The concentration of $K^{\cdot}$ deduced by McBain, Laing, and Titley from conductivity and freezing-point data was $0{\cdot}17N$, and the total concentration of crystalloid $0{\cdot}19N$.

The following table contains the concentrations of all the constituents of this solution.

TABLE XI.

$K^{\cdot}$.	Oleate′.	K oleate.	Micelle.	Neutral colloid.
0·185	(0·003)	(0·002)	0·185	0·415

There is thus considerably more colloid present in potassium oleate than in a corresponding concentration of potassium laurate, the amount of soap present as crystalloid in the former being practically negligible. However, the sodium oleate contains even more neutral colloid than the potassium oleate, and only two-thirds as much micelle and alkali ion.

III. *Sodium Palmitate at* 90°.

The values of V_1, C_1, and E work out at 29 mhos., $0{\cdot}41N$, and 29 millivolts respectively. The corrected electromotive force becomes 2·234 volts, and comparing this with the *E.M.F.* for $0{\cdot}2N$-sodium chloride (2·261 volts), we obtain a concentration of sodium ion of $0{\cdot}40N$.

The total concentration of crystalloid from osmotic data was $0{\cdot}52N$, and the concentration of $Na^{\cdot}$ from conductivity $0{\cdot}37N$. From these figures we obtain the following concentrations of all the constituents of N-sodium palmitate.

TABLE XII.

Crystalloid.			Colloid.	
Na′.	Palmitate′.	Na palmitate.	Micelle.	Neutral colloid.
$0{\cdot}40N$	$0{\cdot}07N$	$0{\cdot}05N$	$0{\cdot}33N$	$0{\cdot}55N$

The formula of the palmitate micelle, assuming that the whole of the neutral colloid is absorbed into the micelle, would be $[(NaP)_{1\cdot7}(P')(H_2O)x]_n$.

The concentration of sodium ion found from conductivity data was originally calculated by assuming the ionic mobility of the micelle to be equal to that of the acetate ion. Now this is not the true mobility of the micelle, but is an average value, made up

of the mobility of the micelle and of the ion. We can, however, calculate the true mobility of the micelle, using the relative concentrations of micelle and ion recorded above. We then find the mobility of the micelle to be 139, which is the same as the mobility of the sodium ion.

Conclusion.

The results of these electromotive force determinations, both from direction and magnitude of the diffusion potential between soap and potassium chloride, as here interpreted (which could be explained in no other way), and further by comparison with known concentration of potassium and sodium chlorides, supports the theory of colloidal electrolytes advanced from this laboratory.

The concentrations of sodium and potassium ions already deduced from a comparison of conductivity data and osmotic activity are confirmed by the direct measurements here presented for a selection of typical cases at 18° and 90°. Gelation (not formation of white curd) of sodium oleate does not influence the results obtained.

I wish to acknowledge grants from the Research Fund of the Chemical Society and from the Colston Society of the University of Bristol, which rendered it possible to carry out this work, which was commenced in 1914.

My thanks are also due to Prof. J. W. McBain for the constant interest he has taken in my work.

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LVII.—*Studies in Emulsions. Part I. A New Method of Determining the Inversion of Phases.*

By SHANTI SWARUPA BHATNAGAR.

THERE are two methods generally in use of determining whether a given emulsion is one of "oil in water" or "water in oil," namely, the colour-indicator method due to Robertson, and the "drop-method" due to Briggs. The former has been found unsatisfactory by Newman (*J. Physical Chem.*, 1914, **18**, 34), and it is also likely that the character and stability of an emulsion might be disturbed by the introduction into the system of an

organic substance like Sudan III, which is used in this method to colour the oil phase.

Further support for this conclusion is derived from the observation of Clowes (*J. Physical Chem.*, 1916, **20**, 445), who finds that organic substances have a very great effect on the size of globules in emulsions. The "drop-method" suffers a disadvantage on account of the fact that a single drop of an emulsion may not always represent the emulsion, whilst if a representative portion of an emulsion is shaken with a large quantity of oil or water, the temporary emulsion due to mechanical shaking may make it extremely difficult to determine the type.

It is sometimes necessary to determine the critical point when one type of emulsion changes into the other. Besides the defects pointed out above, these methods completely fail to give a sharp indication of the critical point, and are therefore not quite convenient for studying the effects of electrolytes and other substances on emulsions. The method which is now described is free from these defects and indicates the critical point very sharply, and is therefore very useful for studying the changes in the inversion point of emulsions by electrolytes and other chemical agents. Besides being a general method, it is found, as shown further, to facilitate the study of de-emulsification and temporary emulsions. The emulsions can be tested by this method as a whole without treating separate portions by frequent removals of samples.

The Method.

The principle of the method is based on the fact that an emulsion of the oil-in-water type, especially when electrolytes are present, would have a much greater electrical conductivity than the other type when oil, an insulating medium, becomes the continuous phase. Preliminary trials of this method were made with emulsions of olive oil (containing 0·5 per cent. of free oleic acid) and dilute aqueous potassium hydroxide solution, and the emulsions so formed were found to be distinctly of two types, one showing marked conductivity and the other very little. In a set of experiments in which the oil was gradually added to the aqueous phase, it was found, as indicated in tables I and II, that the conductivity decreased in a regular manner according to the amount of oil added until a point was reached when any further addition of oil produced a sudden rapid rise in the resistance of the emulsion. This point must be the critical point. A sensitive milliammeter was used to obtain a sharp indication of this point. Results obtained by this method were checked from time to time

by observations under the microscope, and were found to be invariably correct. Some trials were also made on technical emulsions like margarine, and it was found that most of the samples examined showed very little conductivity. The distinct conductivity exhibited by some samples must be attributed to the fact that complete inversion had not taken place in these emulsions.

EXPERIMENTAL.

The emulsions were prepared in wide-mouthed bottles carefully cleaned with hot chromic acid and boiling water. One set of experiments was tried in which the aqueous phase was gradually added to the oil, and the other in which the oil was gradually added to the aqueous phase. Different strengths of different alkali hydroxides were tried. The bottles were shaken for a constant time after each addition in a powerful mechanical shaker, and the total time of shaking was also kept constant to ensure identical conditions. Most of the experiments of Briggs, Robertson, Newman (*loc. cit.*), Donnan (*Zeitsch. physikal. Chem.*, 1897, 31, 42), and Clowes (*loc. cit.*) were repeated and their results examined by this method.

The procedure was as follows. The emulsions in the bottle, after suitable shaking, were examined by inserting two clean platinum electrodes fixed at a constant distance, and a constant voltage was allowed to operate for a moment to see whether the needle of the ammeter showed that the emulsion was conducting. If it showed good conductivity, the emulsion was considered of the oil-in-water type; if not, of the reverse type. In order to examine emulsions in small quantities, or a particular portion or sample of emulsion, the bottle was replaced by a clean T-shaped glass container in which two platinum wires were sealed.

Results.

Newman's work throws doubt on the question of inversion by mere dilution, as he was not able to prepare an emulsion of the water-in-oil type with sodium hydroxide and olive oil. Robertson and others claim to have obtained both types. Since Newman's objection to Robertson's emulsion of the water-in-oil type is based on the argument that the colour-indicator method is defective, some tests were made by the electrical method to decide whether both types of emulsions can be formed by sodium hydroxide or sodium oleate and olive oil. The results are indicated in the tables.

TABLE I.

0·933N/100-Potassium hydroxide: 25 c.c. used in each experiment.

Olive oil containing 0·5 per cent. of oleic acid.

Time for shaking, five minutes after each addition.

Electrodes fixed, constant voltage.

Olive oil.	Readings of ammeter.	Types.
5	13·0	Oil in water (creams).
10	12·7	,, ,,
15	12·5	,,
20	12·35	,,
25	11·85	,,
30	11·45	,,
50	10·65	,,
65	10·4	,,
80	10·0	,,
85	0·1	Water in oil (thick) ←
90	—	Jelly-like.
100	—	,,

TABLE II.

Potassium hydroxide as in table I.

Paraffin oil (B.P.) containing 0·5 per cent. of oleic acid.

Other conditions the same as before.

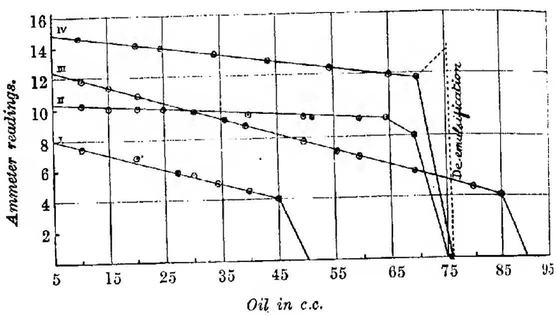
Oil.	Readings on ammeter.	Type.
5	13·2	Oil in water.
10	13·0	,,
15	12·7	,,
20	12·8	,,
25	12·6	,,
30	12·3	,,
35	12·0	,,
37	11·8	,,
40	11·7	,,
45	11·3	,,
46	0·1	Water in oil. ←

Thus the electrical method shows that by increasing additions of oil to the alkali, a point (indicated by the arrow) is reached when the type changes, as is made evident by the sudden fall in the conductivity of the emulsion to practically zero. These falls are entirely different in their abruptness and suddenness from the fall due to the formation of emulsion or to the action of the alkali on the oil. The graphs represent the changes going on before and at the time of inversion. It is found that the water-in-oil type with kerosene oil is very unstable. The emulsion shows no conductivity for a minute or two, and then it gradually rises

until it indicates its previous conductivity. The drops of water, as they de-emulsify, are visible, and are seen to be constantly falling to the bottom, until the emulsion undergoes complete disintegration.

Effects of Bivalent Alkalis.

Some experiments were tried in which solutions of barium and calcium hydroxides were used instead of sodium and potassium hydroxides. The results were very nearly the same as with univalent alkalis up to a certain concentration (about $N/500$), and the formation of the type appeared to depend only on the ratio of the two phases. As the concentration was increased, however,



I. 5 c.c. of 0·1866 N-potassium hydroxide and paraffin oil (B.P.)
II. 25 „ 0·000933 N-potassium hydroxide and olive oil.
III. 10 „ 0·01866 N-potassium hydroxide and olive oil.
IV. 25 „ 0·000933 N-potassium hydroxide and kerosene oil.
Oleic acid in each case, 0·5 per cent.

it was found that the bivalent alkalis promoted the formation of the water-in-oil type of emulsion, and univalent alkalis that of the reverse type, that is, in concentrations greater than $N/500$ the electrolytic effect predominates over the volume-ratio effect of the two phases. These effects are dealt with more quantitatively later on.

The Zone of Instability.

It was found that the inversion point could be reached from both ends. The critical point was, however, reached in a curious fashion when small amounts of the aqueous solution were added to large quantities of oil. A zone of instability made its appearance, when the emulsion separated into three layers—the top one

showing no conductivity, the middle one showing slight conductivity, and the lower portion high conductivity. This zone of instability does not appear when the critical point is reached by adding oil gradually in instalments to large quantities of the aqueous phase.

The probable cause is that when there is present a large quantity of oil containing oleic acid, and the alkali is added in small quantities, the soap formed at the surface between the oil and aqueous solution covers the surface with a thick membrane. This does not dissolve completely in the small amount of water which is present. The surface ceases to be readily mobile, and the spreading out is retarded. Any further additions of the aqueous phase simply settle down under the action of gravity until a sufficient amount of water is accumulated to dissolve the soap membrane. The emulsion, when now shaken, does not divide into three layers. This explanation is further supported by the fact that if the additions of the aqueous phase are large enough, the zone of instability does not seem to make its appearance. Quincke also found that when much alkali is added to a little oleic acid there are obtained oleates more readily soluble in water than when small amounts of alkali are used with much oleic acid.

Stability and Closest Packing.

Walter Ostwald's theoretical considerations on the volumes of the phase ratio at the critical point have been considered to be faulty, as Pickering (T., 1907, **91**, 2001) has been able to obtain emulsions of 99 per cent. of oil and 1 per cent. of water in which oil exists as drops and water as the continuous medium, yet Pickering himself notes that the phase ratios are in most cases in accordance with Walter Ostwald's views of closest packing, and he considers the volume percentage of 74·04 per cent. to be of special significance. Hatschek (*Rep. Brit. Assoc.*, 1918) also notes that all emulsions which separate on standing and have a thin, watery residue yield a stable cream in which oil and water are in the ratio of closest packing, and draws the conclusion that "stability is not complete unless the volume ratios approach the figure corresponding to closest packing."

Robertson was able to emulsify 91·74 per cent. olive oil in 9·26 per cent. alkali, but the strength of the latter was almost $5N$. He observed that with decreasing strength of alkali, the critical points were shifted near to the point of closest packing. If he had tried still weaker alkalis and stabilised his emulsion by following the precautions suggested by Donnan, and by adding

the phases in small instalments as advocated by Bancroft, he would certainly have arrived at the ratio 74:26.

The author finds that the volume percentage of 74·04 holds when the aqueous phase is very weakly alkaline ($N/1000$—$N/500$). With more concentrated alkalis, higher ratios can be obtained, and Robertson's results can generally be repeated. The emulsions prepared with concentrated alkalis break up and a stable cream separates, which again has the volume ratio 74:26.

The phase ratios at the critical point with different strengths of alkalis were found to be:

TABLE IV.

Amount of alkali. C.c.	Amount of olive oil, 0·5 per cent. C.c.	Strength of alkali.	Volume ratio at inversion point.
25	73·5	0·933N/1000	74 : 26
20	58·4	0·933N/700	74·5 : 25·5
25	72·7	0·933N/500	74·4 : 25·6
20	75·2	0·933N/100	79 : 21
10	88·9	0·933N/50	89 : 11

It appears that the volume ratio is disturbed on account of the solid or gelatinous film which may be formed round the enclosed particle when concentrated alkalis are used. This solid can further interfere by preventing the enclosed particles from coalescing and assuming any other size or shape. Further agitations, instead of making the globules more uniform, cause irregularities of shape.

Homogeneous Emulsions of Equal Particles.

Experiments were made in order to obtain homogeneous emulsions of particles of uniform size, and, after a long and careful study, it was found possible to obtain an emulsion in which most of the globules were equal spheres. It has been found that the best way to obtain an emulsion of this character is to select from a freshly prepared oil-in-water emulsion the cream which forms on standing undisturbed, and in which the volume ratios are close to 74:26. Very small quantities, from 5 c.c. to 10 c.c., were placed in a very carefully cleaned resistance-glass bottle and vigorously shaken for several hours by a powerful shaking machine. Samples were examined from time to time under the microscope until the particles were found to be very small and of nearly equal size. It was possible to preserve this character of the emulsion for several hours. It was found absolutely necessary to try these

operations only on freshly prepared emulsions, as emulsions which were allowed to remain for a day did not give such satisfactory results. This may be due to the ageing of the soap film, which makes it harder and more like a solid.

Three such homogeneous emulsions were prepared with different strengths of alkali, and measured quantities were decomposed by a drop of concentrated acid, and the volumes of the two phases measured in the measuring tube. The values of these, calculated from the radii of the globules on the assumption of closest packing and obtained practically, are tabulated in table V, and show a very fair agreement.

TABLE V.

Oil phase calculated from the equation for closest packing,

$$\frac{4\sqrt{2}\times r^3}{4\pi/3r^3} = \frac{\text{Total volume}}{\text{Oil phase}}, \text{ where } r = \text{radius of the globules.}$$

Emulsion.	Total volume. C.c.	Strength of potassium hydroxide.	Radii of uniform particles. Mm.	Oil phase observed. C.c.	Oil phase calculated. C.c.
I.	7	$0{\cdot}933N/500$	0·0075	5·09	5·1
II.	5	$0{\cdot}933N/700$	0·0070	3·7	3·69
III.	5	$0{\cdot}933N/1000$	0·0055	3·6	3·69

The results indicate that a weaker alkali yields a homogeneous emulsion of smaller globules. The size of the globule seems to depend on the concentration of the alkali if the shaking is constant. More work is necessary to establish this, and no conclusions can be drawn until sufficient data are available. It is intended to carry out further work on this important point by preparing larger quantities of homogeneous emulsions.

Effects of Electrolytes on Emulsions.

Clowes (*loc. cit.*) has demonstrated that suitably constituted emulsions of oil dispersed in water can be transformed into the reverse type of emulsions by shaking with a sufficient amount of calcium chloride or other calcium salts. He obtained some quantitative data, but his results are not sufficiently accurate on account of the method by which he studied inversion. A foreign substance like Sudan III had to be added, and the quantity of the emulsion was sensibly affected by the frequent removal of drops for examination under the microscope.

To ensure identical and comparable conditions, equal volumes of paraffin oil (B.P.) and water were used in all the following experiments. The paraffin oil contained 1 per cent. of oleic acid,

1 per cent. stearic and linoleic acids being also used. Emulsions were prepared in the mechanical shaker by shaking together equal volumes of oil and water in which varying proportions of potassium hydroxide and electrolytes were added previous to emulsification. The volume of water and oil was always kept the same. A few results are tabulated below, the details and fuller discussion being reserved for a later contribution.

Table VI.

Effect of potassium hydroxide and barium nitrate on the emulsion equilibrium.

Volume of aqueous phase constant, 10 c.c.; volume of oil, 10 c.c.

Figures in the ammeter column; oil-in-water type.

0—1 = inversion point.

0 = water-in-oil type. Voltage constant. Electrodes fixed.

Volume of $M/50$-KOH c.c.	Volume of $M/50$-$Ba(NO_3)_2$ in c.c.						
	0·2	0·4	0·6	0·8	1·0	1·2	1·4
1	0—1	0	0	0	0	0	0
2	10·2	0—1	0	0	0	0	0
3	11·2	10·8	0—1	0	0	0	0
4	12·1	11·2	10·7	0—1	0	0	0
5	13·0	12·7	11·8	10·9	0—1	0	0
6	14·1	13·0	12·8	17·1	10·7	0—1	0

Milliammeter reading.

Table VII.

Different Strength of the same Electrolyte.

Volume of $M/10$-KOH c.c.	Volume of $M/10$-$Ba(NO_3)_2$ in c.c.							
	0·1	0·25	0·3	0·4	0·6	0·8	1·0	1·5
1	12·1	0—1	0	0	0	0	0	0
2	13·0	12·7	11·9	11·0	0	0	0	0
3	13·9	13·0	12·3	11·9	11·0	0—1	0	0
4	14·6	13·7	13·0	12·1	11·7	—	—	—
5	15·5	14·7	13·9	13·0	12·1	11·9	11·7	0
6	16·3	15·3	14·8	14·0	13·0	12·0	11·7	0—1

Milliammeter reading.

Table VIII.

Linoleic Acid substituted in Place of Oleic Acid in Oil.

Volume of $M/10$-KOH c.c.	Volume of $M/10$-$Ba(NO_3)_2$ in c.c.							
	0·1	0·25	0·3	0·4	0·6	0·8	1·0	1·5
1	12·1	0—1	0	0	0	0	0	0
2	13·1	0—1	0	0	0	0	0	0
3	13·9	13·0	12·8	0—1	0	0	0	0
4	14·2	13·1	12·8	11·9	0	0	0	0
5	15·3	14·8	13·2	12·9	0—1	0	0	0
6	16·3	15·9	14·1	13·4	12·5	0—1	0	0

Milliammeter reading.

Other conditions as in tables VI and VII.

Clowes (*loc. cit.*) finds that emulsions of oil in water are produced whenever there are more than four molecules of sodium hydroxide to one of calcium chloride, emulsions of water-in-oil type whenever there are less than four molecules of the former to one of the latter, whilst at those points at which the ratio of sodium hydroxide to calcium chloride is exactly 4:1, neither type of emulsion predominates. The results indicated in tables VI or VII and VIII show that the ratio of potassium hydroxide to barium nitrate is exactly 4:1 in concentrations ranging from $M/10$-potassium hydroxide upwards. In lower concentrations the ratio is increased; for example, at $M/50$-potassium hydroxide it is about 5:1. Even the acid in oil appears to have some effect on the inversion point; for example, in table VIII, when linoleic acid is substituted for oleic acid, the ratio between potassium hydroxide and barium nitrate molecules is as 2:1. Employing this method, it will be easy to obtain much information on the effects of electrolytes on emulsion equilibrium in different concentrations and with different fatty acids.

These are effects the study of which is of great importance for a general theory of emulsification.

When de-emulsification takes place, the two phases separate and do not form an emulsion. De-emulsification is not easily and immediately detected by the eye, or by the methods of identification previously known. The electrical method is capable of indicating at once whether de-emulsification or coagulation has set in. If, on adding oil to an emulsion, it is found that the conductivity is increasing instead of decreasing, it is clear that the process of emulsification has stopped and the oil and the aqueous phase are separating, that is, de-emulsification has set in.

Further work on the effects of electrolytes on the emulsion equilibrium and the physical properties of emulsion is in progress.

Summary.

(1) A new method for the determination of inversion of phases and the identification of the two types of emulsion is described.

(2) Quantitative data on the effects of a few electrolytes on emulsion equilibrium have been obtained.

(3) The inversion point has been accurately determined with various oils and alkalis.

(4) It has been established that both types of emulsion are formed by sodium hydroxide and olive oil, and by sodium hydroxide and paraffin oil.

(5) Homogeneous emulsions have been obtained, and the equation for closest packing appears to hold in them.

(6) The effect of different fatty acids on the emulsion equilibrium is indicated in passing, details being reserved for a later contribution.

(7) It is shown that with weak alkali hydroxides the conditions governing the formation of type are dependent only on the phase ratio, and the special nature of the emulsifying agent exerts an effect only in high concentrations.

The author has pleasure in thanking Prof. F. G. Donnan for suggesting this research, and for his valuable guidance and kindly interest throughout the work. His thanks are also due to Mr. Higson for measuring the size of particles in homogeneous emulsions.

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LVIII.—*The Decomposition of Nitric Esters by Lime.*

By THOMAS MARTIN LOWRY, KENDALL COLIN BROWNING, and JOSHUA WILLIAM FARMERY.

Earlier Work on the Decomposition of Nitric Esters.

THE decomposition of nitric esters by water, acids, and alkalis has been investigated by many workers.

(*a*) Van Kerckhoff and Reuter (*J. pr. Chem.*, 1847, **40**, 261) studied the decomposition of "pyroxylin" or nitrocellulose by steam at 100°, and obtained as a principal product a "typhoxylin" or "cellulose dinitrate" containing 6·66 per cent. of nitrogen; they also record the separation of a lead salt, which was almost certainly identical with the lead hydroxypyruvate prepared by a similar method and described in detail by Will forty-four years later (*Ber.*, 1891, **24**, 401); by heating pyroxylin with potassium hydroxide at 60°, potassium nitrate, potassium nitrite, and a sugar were formed.

(*b*) The production of potassium acetate and potassium formate, together with potassium nitrate and potassium nitrite in the ratio $KNO_3:2KNO_2$, was recorded by Hay (*Mon. Sci.*, 1873, [iii], **15**. 424), who accounted for the fact that five molecules of potassium

hydroxide were required for the decomposition of one molecule of nitroglycerin by putting forward the equation

$$C_3H_5O_9N_3 + 5KOH = KNO_3 + 2KNO_2 + CH_3{\cdot}CO_2K + H{\cdot}CO_2K + 3H_2O.$$

(*c*) Berthelot (*Compt. rend.*, 1900, **131**, 519) described the production of polymerisation-products of aldehyde by the action of solid potassium hydroxide on ethyl nitrate, and put forward (only to reject it in favour of an alternative view) the suggestion that the formation of nitrites in the action of potassium hydroxide on nitroglycerin might be due to a decomposition of the nitric ester into glyceraldehyde, as shown in the equation

$$C_3H_5(NO_3)_3 + 3KOH = C_3H_6O_3 + 2KNO_3 + KNO_2 + H_2O.$$

(*d*) Silberrad and Farmer (T., 1906, **89**, 1182, 1759) also detected acetic and formic acids, with nitric and nitrous acids, amongst the products of decomposition of 100 kilograms of nitrocellulose which had been stored at 54° during a period of twenty-three weeks; in addition, they proved the presence of ethyl nitrate, ethyl nitrite, and alcohol (perhaps derived from the alcohol–ether mixture used as a solvent in gelatinising the nitrocellulose), of butyric, dihydroxybutyric, oxalic, tartaric, and *iso*saccharic acids, and of a fermentable sugar, but they did not find either glycerol or cellulose amongst the products of decomposition of cordite by water or in presence of alkalis.

(*e*) Berl and Delpy (*Ber.*, 1910, **43**, 1421), by the action of alcoholic potassium hydroxide on nitroglycerin, obtained a glyceryl $\alpha\alpha'$-dinitrate, but were unable to detect either the mononitrate or glycerol itself.

(*f*) Klason and Carlson (*Ber.*, 1906, **39**, 2752), by the action of alcoholic sodium hydroxide on nitroglycerin in the presence of phenyl mercaptan, were able to recover glycerol, the mercaptan being oxidised to phenyl disulphide; by the same method they obtained from nitrocellulose a sample of cellulose of correct composition and free from nitrogen, whilst under similar conditions, ethyl nitrate gave the nitrate and nitrite of the alkali, but no trace of polymerised aldehyde. These observations are in line with the well-known fact that glycerol can be recovered from nitroglycerin by the action of sodium sulphide. A similar action to that of phenyl mercaptan is observed when hydrogen peroxide is added to the mixture (Carlson, *Ber.*, 1907, **40**, 4191); the hydrogen peroxide acts here as a reducing agent, just as it does towards potassium permanganate, and gaseous oxygen is liberated as a by-product.

Products of Decomposition of Cordite by Lime.

During the early months of 1919, the authors of this paper had an opportunity of examining the products obtained by the decomposition of cordite by means of lime in the presence of pyridine. The use of pyridine as a catalyst in this action was discovered by Prof. Hodgkinson, and no other substance is known which is equally effective in promoting the controlled decomposition of cordite. The product is a brown sludge, which can be dried in thin layers on a hot plate to a hard, brittle, porous mass resembling ginger-biscuits. Drying on a large scale is more difficult, but when the sludge is evaporated at a low temperature until it contains only about 17 per cent. of water, it solidifies on cooling, probably owing to the crystallisation of calcium nitrate in the form of the tetrahydrate, $Ca(NO_3)_2,4H_2O$, or the basic compound,

$$Ca(NO_3)_2,CaO,3H_2O$$

(Bassett and Taylor, T., 1914, **105**, 1926); after casting, the solid product will dry spontaneously in a warm atmosphere, and can then be powdered without difficulty.

In addition to ammonia and the oxides of nitrogen, which escape during the decomposition, the following products have been detected in the sludge:

(*a*) "*Cellulose Trinitrate.*"—When a half-decomposed cordite sludge is extracted with water and acid, and the dried residue is warmed with 95 per cent. alcohol and filtered, the addition of water to the alcoholic solution causes the precipitation of a yellowish-white, viscid precipitate, which contains N = 9·6 per cent. and is highly inflammable. A similar substance has been described by Angeli (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 20), who obtained it by the addition of water to a solution of gun-cotton in pyridine (compare also Berl and Fodor, *Zeitsch. ges. Schiess.-u. Sprengstoffw.*, 1910, **5**, 254, 269). The formula $C_{12}H_{17}O_7(NO_3)_3$ requires N = 9·15 per cent.

(*b*) "*Cellulose Dinitrate.*"—Analysis by the Schultze-Tiemann method of black charred rods remaining undecomposed after thirty-three hours' treatment with an insufficient supply of lime showed the presence of 6·7 per cent. of nitrogen as compared with 12·2 per cent. in the original nitrocellulose. The composition of this residue agrees in a remarkable way with the figure obtained by van Kerckhoff and Reuter (*loc. cit.*). The percentage of nitrogen required for the formula $C_{12}H_{18}O_8(NO_3)_2$ or $C_6H_9O_4{\cdot}NO_3$ is 6·76.

From these observations, it appears probable that the nitrocellulose, which contains originally four or five NO_3-groups for every twelve carbon atoms, is hydrolysed in successive stages to

compounds containing three and two nitro-groups, but that after this point has been reached, the molecule decomposes completely.

(c) *Glycerol.*—Prof. Hodgkinson had already shown that glycerol could not be extracted as a by-product from the residues obtained from the decomposition of cordite by lime and pyridine. Careful tests for the presence of glycerol were, however, carried out, in order to ascertain whether the toxicity to plants, which Dr. Russell reported in some of the earlier products, might not be due to the presence of glycerol in quantities insufficient for commercial recovery. A highly toxic solution obtained after forty-eight hours' treatment was found to contain no glycerol, and its toxicity was traced to the hydroxypyruvic acid which it contained (see below). A similar negative result was obtained on examining a sludge which had been heated during a period of only ten hours, at which stage practically all the nitroglycerin had disappeared, whilst most of the nitrocellulose was left unattacked in the form of brittle, porous rods.

In order to determine whether glycerol could be detected amongst the earliest products of decomposition, a special batch of sludge was prepared by heating, for one hour only at 95° to 100°, 450 grams of cordite clippings with the usual proportion of quicklime (225 grams), but using a very large excess of pyridine, namely, 4 litres of a 5 per cent. solution, that is, 44 per cent. of pyridine on the weight of cordite used instead of the usual proportion of 0·5 per cent. The decomposition was extremely rapid and complete; no traces of cordite could be seen at the end of one hour, and it was estimated that the action had proceeded at least as far as in twenty-four hours of treatment under ordinary conditions. The filtrate from this sludge was tested for glycerol, and traces of this compound were detected by the following tests:

(i) A drop of phenolphthalein was added to a 5 per cent. solution of borax; on adding the suspected liquid, the red colour was discharged, and, on boiling, it partly returned.

(ii) On heating the dry residue with potassium hydrogen sulphate, the choking odour of acrolein was noticed.

(iii) On heating with alkaline potassium permanganate, a partial reduction occurred.

(d) *Calcium Nitrate and Nitrite.*—A sample of sludge prepared by a similar method from 900 grams of cordite (with 22 per cent. of its weight of pyridine), after one hour's heating, gave for the first time an excellent yield of colourless, crystalline calcium nitrate. It is therefore possible that the action of pyridine on cordite differs from that of alkalis and of lime in giving an appreci-

able quantity of the products of direct hydrolysis, namely, glycerol and nitrates, and a much smaller proportion both of nitrites and of oxidised organic compounds; in other words, the decomposition by pyridine may perhaps be compared with that effected by alkali sulphides rather than by alkali hydroxides or by lime. The presence of nitrites is shown by the invariable liberation of oxides of nitrogen on acidifying the sludge.

(*e*) *Oxalic Acid.*—The fraction of the calcium salts which was soluble in hot dilute nitric acid, but insoluble in acetic acid, gave, after prolonged purification, a crystalline specimen of oxalic acid. A quantitative test by oxidation with potassium permanganate indicated that the calcium salts insoluble in acetic acid contained 62 per cent. of calcium oxalate.

(*f*) *Formic and Acetic Acids.*—Qualitative tests for these two acids gave in each case a positive result in only one of the tests applied, the other tests giving negative results. It is therefore clear that they can only have been present in very minute proportions, and that Hay's equations represent only a very minor part of the particular decomposition which we have studied.

(*g*) *Hydroxypyruvic Acid*, $HO\cdot CH_2\cdot CO\cdot CO_2H$.—After calcium oxalate and calcium nitrate and nitrite, the calcium salt of this acid appears to be the most important product of decomposition. Will prepared it by the decomposition of nitrocellulose, and it does not appear to have been described as a separate product of decomposition from nitroglycerin; on the other hand, the fact that it appears at a very early stage in the decomposition of cordite by lime and pyridine, and tends to disappear during the latter part of the decomposition, suggests that in this action it may be derived, at least in part, from nitroglycerin, to which it can be related by very simple equations.

Hydroxypyruvic acid was found to be present in every case in which the products of decomposition of cordite were reported as having a toxic action on plants, and a specimen of the calcium salt sent to Rothamsted for trial was reported as being extremely toxic. The presence of the acid was confirmed by preparing the osazone.

(*h*) *βγ-Dihydroxybutyric Acid.*—The residue from the preparation of the osazone, after removing the excess of phenylhydrazine by extraction with ether, can be re-precipitated as a lead salt and then converted into a calcium salt. This has the properties of the calcium salt of dihydroxybutyric acid (Silberrad and Farmer, *loc. cit.*), that is, the calcium salt is soluble, but gives an insoluble lead salt and does not yield an osazone; unlike the

hydroxypyruvate, this calcium salt was proved not to be toxic to plants.

The two calcium salts described under (*g*) and (*h*), instead of appearing as mere traces, like the formate and acetate, are often formed in considerable quantities, and in one experiment alone a test-tube full of the mixed lead salts was separated.

Decomposition of Nitric Esters not a Simple Hydrolysis.

The object of bringing forward these observations and comparing them with earlier work on the same subject is to direct attention to the wide divergence between the experimental facts and the traditional theory in which the decomposition of nitric esters by alkalis is described as if it were a normal case of the hydrolysis of an ester complicated only by secondary processes of oxidation and reduction of the primary products.

The absence of glycerol as a product of decomposition of cordite is specifically referred to by Silberrad and Farmer, who made experiments under a variety of conditions, and also by Berl and Delpy in their study of the action of alcoholic potassium hydroxide on nitroglycerin. Prof. Hodgkinson also noticed at a very early period of his experiments that glycerol cannot be recovered as a product of the decomposition of cordite by lime in the presence of a small proportion of pyridine. Our own experiments fully confirm this conclusion, and a recent French patent, in which it was claimed that glycerol as well as sodium nitrate could be recovered from the products of the action of sodium hydroxide on mixtures of nitrocellulose and nitroglycerin "by the ordinary methods of the soap-manufacturer," was based on experiments with nitrocellulose powders only, and must be regarded as evidence rather of the optimism of the inventor than of the actual behaviour of nitroglycerin towards sodium hydroxide. The general experience seems to be that, in the absence of a reducing agent, glycerol is not regenerated.

This anomalous behaviour of nitroglycerin is repeated in nitrocellulose, which does not give any cellulose when decomposed by water or by alkalis (Silberrad and Farmer), as well as in simpler compounds, such as ethyl nitrate.

In order to account for this anomaly, whilst maintaining the view that the fundamental action is a hydrolysis or saponification of the normal type, a number of hypothetical reactions have been postulated. Thus, Silberrad and Farmer found it "somewhat surprising that no unchanged cellulose or glycerol should be

regenerated on hydrolysis, for if nitric acid is brought into contact with cellulose or glycerol in the concentrations which come into consideration in the hydrolysis, no oxidation occurs." They were therefore driven to the conclusion "that the nitric acid which has just been set free from the nitric ester is in a more active condition than nitric acid in its ordinary form."

In a similar way, Hay explained the production of potassium nitrate, nitrite, acetate, and formate by the action of potassium hydroxide on nitroglycerin as due to three consecutive actions, the second of which (a decomposition of glycerol by potassium hydroxide) is purely hypothetical, thus:

(i) A primary hydrolysis producing glycerol and potassium nitrate according to the equation

$$C_3H_5(NO_3)_3 + 3KOH = C_3H_8O_3 + 3KNO_3.$$

(ii) A hypothetical action, whereby the glycerol was converted by the action of the alkali hydroxide into potassium acetate and formate, together with water and "nascent hydrogen,"

$$C_3H_8O_3 + 2KOH = CH_3{\cdot}CO_2K + H{\cdot}CO_2K + H_2O + 4H,$$

using up two additional equivalents of potassium hydroxide (above those required for hydrolysis), as observed in his experiments.

(iii) A reduction by the nascent hydrogen of two-thirds of the potassium nitrate already produced,

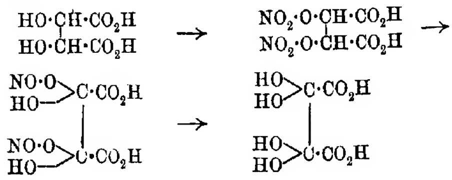
$$2KNO_3 + 4H = 2KNO_2 + 2H_2O.$$

Alternative Explanations of the Decomposition of Nitric Esters.

(*a*) As an alternative to the hypothetical "hydrolysis" represented by the equation

$$R{\cdot}CH_2{\cdot}O{\cdot}NO_2 + KOH = R{\cdot}CH_2{\cdot}OH + KNO_3,$$

Vignon and Maquenne (*Ann. Chim. Phys.*, 1891, [vi], **24**, 522) have assumed the intermediate formation and decomposition of an isomeric nitrite, $R{\cdot}CH(OH){\cdot}O{\cdot}NO$, which, by direct hydrolysis, would give rise to nitrous acid and a dihydroxy- (or carbonyl) compound, so that, for instance, the conversion of nitrotartaric acid into dihydroxytartaric acid may be represented by the following scheme:



This hypothesis has the disadvantage that no evidence has been produced of the concrete existence of the isomeric nitrite, and on many grounds we prefer the alternative views set out under (*b*) and (*c*) below. The paper is, however, important on account of the clear recognition by the authors of the fact that the decomposition of a nitric ester by an alkali may yield a ketone and a nitrite, instead of giving an alcohol and a nitrate as the primary products of decomposition.

(*b*) This alternative hypothesis was put forward in its simplest possible form in 1900 by Berthelot, who suggested that the decomposition of a nitric ester may proceed according to the equation

$$R{\cdot}CH_2{\cdot}O{\cdot}NO_2 + NaOH = R{\cdot}CHO + NaNO_2 + H_2O,$$

in place of the traditional equation

$$R{\cdot}CH_2{\cdot}O{\cdot}NO_2 + NaOH = R{\cdot}CH_2{\cdot}OH + NaNO_3.$$

Our own experiments, confirming as they do the observations of earlier workers, indicate that Berthelot's equation actually represents the main course of the decomposition; indications of a real hydrolysis are apparently confined to the production, as by-products, of partly hydrolysed compounds, such as Berl and Delpy's dinitrate and the lower cellulose nitrates described in the early part of the present paper.

(*c*) An elaboration of Berthelot's view was put forward a few years later by Klason and Carlson (*loc. cit.*), who suggested that the primary products are not the alcohol and a nitrate, thus:

$$C_2H_5{\cdot}O{\cdot}NO_2 + KOH = C_2H_5{\cdot}OH + KNO_3,$$

but an alcohol–peroxide and a nitrite,

$$C_2H_5{\cdot}O{\cdot}NO_2 + KOH = C_2H_5{\cdot}O{\cdot}OH + KNO_2.$$

In the ordinary course of events, the peroxide will decompose into an aldehyde and water,

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}OH = CH_3{\cdot}CHO + H_2O;$$

but when a reducing agent, such as phenyl mercaptan, is present, the peroxide is reduced to the alcohol and the mercaptan is oxidised to phenyl disulphide,

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}OH + 2C_6H_5{\cdot}SH = CH_3{\cdot}CH_2{\cdot}OH + H_2O + (C_6H_5)_2S_2.$$

In the same way, when hydrogen peroxide is present, the peroxide may be reduced to the alcohol, as shown in the equation

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}OH + H_2O_2 = CH_3{\cdot}CH_2{\cdot}OH + H_2O + O_2.$$

(*d*) If it be assumed that the primary decomposition of a nitric ester yields either a peroxide or an aldehyde, together with a nitrite, instead of an alcohol and a nitrate, it is easy to account for many of the products which have actually been obtained by the decomposition. Thus, in the case of nitroglycerin, complete

decomposition on these lines would give rise to a compound containing three carbonyl groups:

$$C_3H_5(NO_3)_3 = CHO{\cdot}CO{\cdot}CHO + 3HNO_2.$$

From this intermediate compound, mesoxalic acid, reported by Berl and Delpy as a product of "hydrolysis" of nitroglycerin by alcoholic potassium hydroxide, could be produced by the normal oxidation of an aldehyde to an acid,

$$CO(CHO)_2 + O_2 = CO(CO_2H)_2;$$

the further oxidation of mesoxalic acid would yield oxalic acid, a principal product of decomposition in the case which we have studied. Hydroxypyruvic acid (the formation of which has, however, been recorded only in the case of nitrocellulose and of cordite, and not from pure nitroglycerin) could be produced by a mere addition of the elements of water to the intermediate product formulated above:

$$CO(CHO)_2 + H_2O = HO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H.$$

(*e*) In our experiments, the decomposition of nitroglycerin into acetic and formic acids takes place only to a very minute extent. The formation of traces of formic acid from the oxidised compounds set out above can be explained readily, but the production of acetic acid is a far more startling type of decomposition, since the formation of the methyl group in acetic acid necessarily involves a process of reduction in a medium in which the conditions appear to favour the oxidation rather than reduction of the organic constituents. It is conceivable that acetic acid and formic acid may be produced by the decomposition of pyruvic acid, formed by reduction from hydroxypyruvic acid,

$$CH_3{\cdot}CO{\cdot}CO_2H + 2KOH = CH_3{\cdot}CO_2K + H{\cdot}CO_2K + H_2O.$$

There is, however, more evidence for the decomposition of this acid into acetaldehyde and carbon dioxide,

$$CH_3{\cdot}CO{\cdot}CO_2H = CH_3{\cdot}COH + CO_2,$$

a change which has been postulated as an essential stage in alcoholic fermentation. In any case, the simultaneous oxidation and reduction which leads to the conversion of dextrose into carbon dioxide and alcohol finds strong analogies in the production, not only in the case of acetic acid, but also of butyric and dihydroxybutyric acids as products of the decomposition of nitrocellulose, since both of these acids agree with acetic acid in containing a fully-reduced methyl or methylene group.

Summary.

(1) Hydrolysis or saponification of the normal type is not the predominant action when cordite is decomposed by lime in the presence of pyridine.

(2) Traces of glycerol were detected only when a very large excess of pyridine was used; these conditions were also the only ones in which a clean, crystalline calcium nitrate was obtained. The calcium salt of hydroxypyruvic acid is, however, an important product of the action.

(3) Two partly denitrated celluloses, corresponding approximately with the formulæ $C_{12}H_{18}O_8(NO_3)_2$ and $C_{12}H_{17}O_7(NO_3)_3$, were obtained as by-products of incomplete decomposition, but no cellulose was obtained when the decomposition was carried to completion.

(4) It is therefore suggested that the main action is a decomposition of the nitric ester into a ketone or aldehyde and a nitrite, instead of a hydrolysis to an alcohol and nitric acid.

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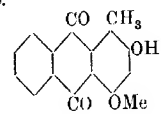
LIX.—*Note on the Constituents of* Morinda citrifolia.

By JOHN LIONEL SIMONSEN.

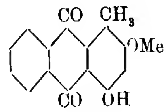
ALTHOUGH a number of investigations have been made of the constituents of *Morinda citrifolia* (compare T., 1918, **113**, 766), particularly by Oesterle, alone or in conjunction with Tisza (*Arch. Pharm.*, 1907, **245**, 287, 534; 1908, **246**, 150), no detailed examination of the root-bark of this species comparable with those conducted by Perkin and Hummel (T., 1894, **65**, 851) on *M. umbellata* and by Barrowcliff and Tutin on *M. longiflora* (T., 1907, **91**, 1909) has yet been made, and the author has thought it desirable to undertake this work.

It is necessary here to draw attention to a curious error in Barrowcliff and Tutin's communication. The hydroxymethoxymethylanthraquinone, melting at 290°, isolated by them, which yielded an acetyl derivative melting at 173°, is not, as they state, derived from 1:3-dihydroxy-2-methylanthraquinone, but is the monomethyl ether of rubiadin, since on hydrolysis it yielded a

dihydroxymethylanthraquinone, melting at 290°, which gave an acetyl derivative melting at 225° (compare Schunck and Marchlewski, T., 1894, **65**, 182). 1:3-Dihydroxy-2-methylanthraquinone also melts at 290°, but yields an acetyl derivative melting at 217—218°. It follows, therefore, that the hydroxymethoxymethylanthraquinone obtained by Barrowcliff and Tutin must be represented by either formula I or II, whilst the so-called 1:3-dimethoxy-2-methylanthraquinone is rubiadin dimethyl ether, 1:3-dimethoxy-4-methylanthraquinone.



(I.)



(II.)

The material available for investigation was the residue remaining after the extraction of morindin (T., 1918, **113**, 766).

Only two substances, namely, rubiadin monomethyl ether and alizarin α-methyl ether, could be isolated from the complex mixture which contained much resinous matter. The rubiadin monomethyl ether was identical with the substance isolated by Barrowcliff and Tutin from *M. longiflora*, and so far as the author is aware this substance has not been obtained from any other source. Alizarin α-methyl ether was first isolated by Perkin and Hummel (T., 1893, **63**, 1174) from *Oldenlandia umbellata*, and subsequently prepared synthetically by Oesch and Perkin (P., 1914, **30**, 213), whilst Barrowcliff and Tutin obtained it from *M. longiflora*.

The identity of the constituents of the root-bark of two plants so closely related as *M. citrifolia* and *M. longiflora* is of considerable interest. It is possible that the latter might at some period of its growth contain morindin, since the quantity of this glucoside appears to vary with the age of the bark. Thus the author has recently examined a specimen of *M. umbellata* which was quite free from colouring matter.

EXPERIMENTAL.

The material used for investigation was obtained by the acidification of the cold and hot water extracts of the sparingly soluble barium salt of morindin (compare Perkin and Hummel, *loc. cit.*, p. 858). The amorphous, yellow precipitates obtained in this way were examined separately, but as the constituents were found to be identical, except that the product precipitated from the hot water extract contained a large quantity of uncrystallisable resinous

matter, it is only necessary to describe in detail the investigation of the products isolated from the cold water extract.

The deep red aqueous solution of the barium salt was acidified with dilute hydrochloric acid, the solution boiled, and the flocculent, yellow precipitate allowed to settle, collected, and drained. After finely grinding and sifting, it was extracted with ether.* The ethereal extract was concentrated when, on keeping, a small quantity of a yellow solid (*A*) separated. This was collected, and the filtrate evaporated to dryness. The semi-solid residue was dissolved in the minimum quantity of hot methyl alcohol and allowed to remain for some days, when a yellow solid (*B*) was slowly deposited. This was collected, and the filtrate (*C*) reserved for further investigation (see below).

The yellow, semi-crystalline substances, *A* and *B*, which melted indefinitely at about 210°, were mixed and repeatedly crystallised first from alcohol and finally from acetic acid. In this manner golden-yellow needles were obtained which melted at 291° (0·1021 gave 0·2672 CO_2 and 0·0414 H_2O. C=71·4; H=4·5. $C_{16}H_{12}O_4$ requires C=71·6; H=4·5 per cent.).

This substance was clearly identical with the hydroxymethoxymethylanthraquinone (rubiadin monomethyl ether) described by Barrowcliff and Tutin (*loc. cit.*, p. 1912), who give the melting point as 290°. This was confirmed by the preparation of the acetyl derivative, which separated from ethyl acetate in long, yellow needles melting at 174° (Barrowcliff and Tutin give 173°). For analysis it was dried at 110° (0·11 gave 0·282 CO_2 and 0·0444 H_2O. C=69·9; H=4·5. $C_{18}H_{14}O_5$ requires C=69·7; H=4·5 per cent.).

For the conversion of the rubiadin monomethyl ether into rubiadin the following method was found to yield the most satisfactory results. The ether (0·5 gram) was mixed with concentrated hydrochloric acid (5 c.c.) and heated for two hours in a sealed tube at 140—150°. The crude product was collected, and boiled with an aqueous solution of barium hydroxide, when the sparingly soluble barium salt of rubiadin separated. This was decomposed with dilute hydrochloric acid, and the rubiadin purified by crystallisation from alcohol, when it was obtained in needles melting at 290° and yielding an acetyl derivative which separated from ethyl acetate in fine, yellow needles melting, as stated by Schunck and Marchlewski (*loc. cit.*, p. 184), at 225°.

The methyl-alcoholic filtrate (*C*), from which the rubiadin methyl ether had been separated, was evaporated to dryness, and the red, resinous residue acetylated by boiling with acetic anhydride contain-

* The residue consisted of resinous matter from which nothing crystalline could be isolated.

ing a drop of pyridine. After removing the acetic anhydride, the crude acetyl derivative was triturated with much ether, when a quantity of a yellow solid remained undissolved. This was separated, the ethereal solution, after washing with sodium carbonate solution which removed a little resinous matter, concentrated and allowed to remain, when a further quantity of a yellow solid was deposited. This was collected and mixed with the yellow solid mentioned above. The filtrate on further concentration yielded only resinous substances, from which nothing crystalline could be isolated.

The yellow acetyl derivative was purified by repeated crystallisation, first from alcohol, and finally from ethyl acetate, when it was obtained in silky, yellow needles melting at 209—210°, and evidently consisted of the acetyl derivative of alizarin monomethyl ether (Perkin and Hummel, T., 1893, **63**, 1174; Barrowcliff and Tutin, *loc. cit.*, p. 1914) (Found, C=69·1; H=4·1. $C_{17}H_{12}O_5$ requires C=68·9; H=4·0 per cent.).

On hydrolysis the acetyl derivative yielded alizarin α-methyl ether, which melted at 177—178°, and the latter when boiled with an aqueous solution of barium hydroxide gave alizarin, which was recognised by the usual tests.

The author wishes to thank Mr. M. Gopal Rau for his assistance.

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LX.—*Syntheses with the Aid of Monochloromethyl Ether. Part IV. The Condensation of Ethyl Benzyl Sodiomalonate and Monochloromethyl Ether.*

By JOHN LIONEL SIMONSEN.

THE conversion of substituted ethyl benzylacetates into derivatives of hydrindene takes place with comparative ease. Thus, Mitchell and Thorpe (T., 1910, **97**, 2263) have shown that ethyl *o*-cyanobenzylmalonate (I), when warmed with a trace of sodium ethoxide in alcoholic solution, is converted quantitatively into ethyl 1-imino-

hydrindene-2-carboxylate (II), which, on treatment with hydrochloric acid, yields ethyl 1-hydrindone-2-carboxylate (III).

$$\underset{\text{(I.)}}{C_6H_4{<}\begin{matrix}CN\\ CH_2\cdot CH(CO_2Et)_2\end{matrix}} \rightarrow \underset{\text{(II.)}}{C_6H_4{<}\begin{matrix}C(:NH)\\ CH_2\end{matrix}{>}CH\cdot CO_2Et} \rightarrow$$

$$\underset{\text{(III).}}{C_6H_4{<}\begin{matrix}CO\\ CH_2\end{matrix}{>}CH\cdot CO_2Et}$$

It appeared to the author to be a matter of some interest to investigate the properties of *ethyl benzylmethoxymethylmalonate* (IV), since it seemed possible that this ester might on hydrolysis lose methyl alcohol, with the formation of hydrindene-2-carboxylic acid (V).

$$\underset{\text{(IV.)}}{C_6H_4{<}\begin{matrix}H\quad MeO\cdot CH_2\\ CH_2 \text{——} C(CO_2Et)_2\end{matrix}} \rightarrow \underset{\text{(V.)}}{C_6H_4{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}CH\cdot CO_2H}$$

The required ester was readily obtained in an excellent yield by the condensation of ethyl benzylsodiomalonate and monochloromethyl ether. On hydrolysis with alcoholic potassium hydroxide, it gave *benzylmethoxymethylmalonic acid*, which decomposed at 160—162°, with the formation of *β-phenyl-α-methoxymethylpropionic acid*. All attempts to convert the methoxy-acid into the hydrindenecarboxylic acid were unsuccessful. When heated with concentrated hydrochloric acid, *α-benzylacrylic acid* was obtained, and the same acid was formed when ethyl benzylmethoxymethylmalonate or benzylmethoxymethylmalonic acid were heated with mineral acids.

It is clear from the above that ethyl benzylmethoxymethylmalonate shows properties similar to those of the methoxymethyl esters described in Part III of this series (T., 1915, **107**, 783), and shows no tendency to undergo ring-formation on hydrolysis. It had been intended to extend these experiments to derivatives of ethyl benzylmalonate with negative groups in the aromatic nucleus, but as there is little prospect of the author being able to continue the work in the near future, it has appeared desirable to publish the results obtained in their present, somewhat incomplete, form.

Experimental.

Ethyl Benzylmethoxymethylmalonate (IV).

Ethyl benzylmalonate (25 grams) was gradually added to finely divided sodium (2·3 grams) suspended in dry ether (200 c.c.), when the sodium rapidly dissolved and a clear solution of the sodium

compound of ethyl benzylmalonate was obtained. Monochloromethyl ether (8 grams) dissolved in twice its volume of dry ether was cautiously added, when a vigorous reaction took place, which was controlled by cooling in ice-water. Next day water was added to dissolve the colloidal sodium chloride, the ether separated, dried, and evaporated. The residual oil was distilled under diminished pressure, when practically the whole passed over at 194—200°/18 mm. On redistillation, the oil boiled constantly at 194—195°/19 mm. (yield, 23 grams):

0·0988 gave 0·2358 CO_2 and 0·0676 H_2O. C=65·1; H=7·6.
$C_{16}H_{22}O_5$ requires C=65·3; H=7·5 per cent.

This ester was obtained as a very viscid oil, which, on keeping for some weeks, crystallised in massive plates melting at about 49—50°. Owing to its ready solubility in all the ordinary organic solvents, it was not found possible to recrystallise it.

Hydrolysis of Ethyl Benzylmethoxymethylmalonate. I. *With Potassium Hydroxide. Benzylmethoxymethylmalonic Acid.*

In performing this hydrolysis, the ester (5 grams) was mixed with methyl-alcoholic potassium hydroxide solution (2·5 grams of KOH) and allowed to remain in the cold overnight, when a sparingly soluble *potassium* salt (*A*) separated in fine needles. This was washed with a little methyl alcohol, and the filtrate heated on the water-bath for one hour, when a further quantity of the potassium salt separated, which was added to *A*.*

The potassium salt was dissolved in water and the solution faintly acidified with hydrochloric acid, when an acid separated as a viscid oil, which rapidly crystallised, and was recrystallised from a mixture of ether and light petroleum:

0·0886 gave 0·1952 CO_2 and 0·0495 H_2O. C=60·1; H=6·2.
$C_{12}H_{14}O_5$ requires C=60·5; H=5·9 per cent.

Benzylmethoxymethylmalonic acid crystallised in stellate needles decomposing at 160—162°. It was readily soluble in ether, chloroform, or benzene, but only sparingly so in water or light petroleum. It yielded a sparingly soluble, amorphous *barium* salt; the *calcium* salt was obtained as a sparingly soluble, caseous, white precipitate, which appeared to be microcrystalline:

* The filtrate from the potassium salt was saturated with carbon dioxide, the alcohol removed on the water-bath, and the aqueous solution acidified, when an oil separated which partly solidified. The solid was collected and found to consist of benzylmethoxymethylmalonic acid. The oily acid was obtained in too small a quantity for investigation.

0·7088 lost 0·2121 H_2O at 120°. H_2O=29·9.
0·3123 gave 0·1068 $CaSO_4$. Ca=10·0.
$C_{12}H_{12}O_5,6\frac{1}{2}H_2O$ requires H_2O=29·9; Ca=10·2 per cent.

0·1029 Gram neutralised 0·0735 gram of barium hydroxide, whereas a dibasic acid, $C_{12}H_{14}O_5$, should neutralise 0·074 gram.

As has been mentioned above, benzylmethoxymethylmalonic acid melted with decomposition, this being due to loss of carbon dioxide with the formation of the monobasic acid, *β-phenyl-α-methoxymethylpropionic acid*. This acid has, so far, only been obtained as a viscid oil. In one experiment, the dibasic acid (0·775 gram) was heated at 165° until all evolution of carbon dioxide had ceased, when a loss in weight of 0·142 gram was observed, whereas this weight of a dibasic acid should lose 0·139 gram in passing to a monobasic acid. A further proof of the formation of the monobasic acid was furnished by the analysis of the *silver* salt, which separated from a faintly alkaline solution as a granular, white powder:

0·1991 gave 0·0727 Ag. Ag=36·5.
$C_{11}H_{13}O_3Ag$ requires Ag=35·9 per cent.

When benzylmethoxymethylmalonic acid was boiled for some hours with hydrochloric acid (50 per cent.), it was converted into *α-benzylacrylic acid* (see below), and this was found to be the simplest method for the preparation of this acid.

II. *With Hydrochloric Acid.* *α-Benzylacrylic Acid*, $CH_2Ph\cdot C(:CH_2)\cdot CO_2H$.

Ethyl benzylmethoxymethylmalonate was hydrolysed by hydrochloric acid only with great difficulty. The ester (20 grams) was mixed with hydrochloric acid (100 grams), acetic acid (25 grams), and water (50 c.c.), and the mixture heated under reflux for thirty-six hours. The oil was dissolved in ether, and the acid removed from the ethereal solution by washing with sodium carbonate solution, from which, on acidification, 2·5 grams of an oily acid* were obtained. The ether was evaporated, and the residual oil mixed with methyl-alcoholic potassium hydroxide solution (7 grams of KOH), when, on keeping, the sparingly soluble potassium salt of benzylmethoxymethylmalonic acid separated. The filtrate from this salt was saturated with carbon dioxide, the alcohol removed by evaporation, and the aqueous solution rendered just acid with hydrochloric acid, when an oil separated which rapidly solidified.

* The oily acid partly solidified and, after draining on porous porcelain, the crystals were found to consist of α-benzylacrylic acid.

The solid was purified by repeated crystallisation from dilute methyl alcohol:

0·1586 gave 0·43 CO_2 and 0·0876 H_2O. C=73·8; H=6·1.

$C_{10}H_{10}O_2$ requires C=74·1; H=6·1 per cent.

a-Benzylacrylic acid separated in glistening prisms, which melted at 68—69°. It was readily soluble in all the ordinary organic solvents, but only very sparingly so in water.

On titration, 0·1109 gram neutralised 0·0589 gram of barium hydroxide, whereas a monobasic acid, $C_{10}H_{10}O_2$, should neutralise 0·0587 gram.

That this acid was not identical with the isomeric α-methylcinnamic acid melting at 74° was shown by the fact that a mixture of the two melted at 40°. Further, these two acids are readily distinguished in that α-benzylacrylic acid yields a readily soluble barium salt, whereas the barium salt of α-methylcinnamic acid is only sparingly soluble.

In alkaline solution, α-benzylacrylic acid is unstable towards potassium permanganate; when dissolved in chloroform, it readily absorbs bromine, with considerable evolution of heat. In one experiment, the acid (0·5 gram) was dissolved in chloroform (3 c.c.) and treated with the calculated quantity of bromine in chloroform solution. On keeping, the *bromo*-acid separated, and was purified by crystallisation either from chloroform or dilute acetic acid:

0·1196 gave 0·14 AgBr. Br=49·8.

$C_{10}H_{10}O_2Br_2$ requires Br=49·7 per cent.

*αβ'-Dibromo-β-phenyl*iso*butyric acid*, $CH_2Ph\cdot CBr(CH_2Br)\cdot CO_2H$, crystallised in fine needles melting at 145—146°. When reduced with sodium amalgam, it yielded β-phenyl*iso*butyric acid, which was identified by conversion into the characteristic amide melting at 107°, and this melting point was not altered by admixture with a specimen of the amide from another source (Found: N=8·6. Calc.: N=8·5 per cent.).

*β'-Bromo-β-phenyl*iso*butyric Acid.*—This acid was formed when α-benzylacrylic acid was mixed with an acetic acid solution of hydrogen bromide (saturated at 0°) and heated in a sealed tube at 100° for two hours. On pouring into water, a heavy oil separated, which was dissolved in ether, the ethereal solution washed to remove acetic acid, dried, and evaporated, when a viscid oil was obtained. After remaining for some days in a vacuum desiccator, it was analysed, and was evidently nearly pure:

0·1455 gave 0·1037 AgBr. Br=30·3.

$C_{10}H_{11}O_2Br$ requires Br=32·9 per cent.

The bromo-acid dissolved readily in potassium hydroxide solution or ammonia, but, on warming, the solution clouded, owing probably to the separation of the hydrocarbon; the acid was, however, much more stable than its isomeride (see below).

When dissolved in concentrated aqueous ammonia and allowed to remain for some days in the cold, it was converted quantitatively into *β′-amino-β-phenyl*iso*butyric acid*. For analysis, it was recrystallised from chloroform:

0·1587 gave 11·6 c.c. N_2 at 32° and 760 mm. N = 7·8.

$C_{10}H_{13}O_2N$ requires N = 7·8 per cent.

This acid separated from chloroform in glistening leaflets melting at 128°. It was readily soluble in water or alcohol, more sparingly so in the ordinary organic solvents.

*β-Bromo-β-phenyl*iso*butyric Acid*, $CHBrPh\cdot CHMe\cdot CO_2H$. —For purposes of comparison, this bromo-acid, which does not appear to have been described previously, was prepared from α-methylcinnamic acid by the action of an acetic acid solution of hydrogen bromide in the manner described above. On pouring the mixture into water, a solid separated, which crystallised from formic acid in glistening prisms melting at 168—170°:

0·1347 gave 0·1037 AgBr. Br = 32·7.

$C_{10}H_{11}O_2Br$ requires Br = 32·9 per cent.

Like other β-bromo-acids, this acid reacted very readily with alkalis. When dissolved in cold sodium carbonate solution, the solution rapidly clouded, with the separation of an oil, and the same behaviour was observed with ammonia, so that it was not found possible to prepare the amino-acid.

In one experiment, the oil formed by the action of dilute sodium carbonate solution was separated, dissolved in chloroform, and treated with a chloroform solution of bromine, when, on allowing the solvent to evaporate, needles were obtained which melted at 65—66°, and evidently consisted of the dibromide derived from allylbenzene, which had resulted from the action of the alkali on the bromo-acid (Found: Br = 57·9. Calc.: Br = 57·5 per cent.).

The author wishes to thank Mr. M. Gopal Rau for assistance in the analytical work.

FOREST RESEARCH INSTITUTE AND COLLEGE,
DEHRA DUN, INDIA. [*Received, April 8th*, 1920.]

LXI.—*The Constituents of Indian Turpentine from* Pinus longifolia, *Roxb. Part I.*

By John Lionel Simonsen.

The manufacture of turpentine in India from the oleo-resin of *Pinus longifolia*, Roxb., is now an established industry, and large quantities of the oil are distilled in the Government factories at Jallo in the Punjab and Bareilly in the United Provinces. The oil, whilst quite suitable for the majority of technical purposes, is regarded as inferior to American turpentine, owing to the residue which it leaves on evaporation and to its proneness to oxidation.

The constituents of Indian turpentine have already formed the subject of several investigations (Rabak, *Pharm. Rev.*, 1905, **23**, 229; Schimmel's *Bericht*, April, 1906, 66; October, 1911, 93; *Bull. Imp. Inst.*, 1911, **9**, 8; Robinson, P., 1911, **27**, 247; Singh, *Ind. For. Rec.*, 1912, **4**, Pt. I), which have established the presence of *l*-α-pinene, β-pinene, a terpene yielding sylvestrene hydrochloride when treated with hydrogen chloride, and a sesquiterpene. Although in the literature it is definitely stated that sylvestrene is present (compare Parry, "Essential Oils," Vol. I, p. 18), yet Robinson (*loc. cit.*), to whom we owe the most careful investigation of the oil that has been made up to the present, drew the conclusion that the fraction previously assumed to contain sylvestrene in all probability contained some isomeric terpene, which on treatment with hydrogen chloride yielded sylvestrene hydrochloride. He also suggested that dipentene was probably present.

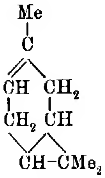
In view of the above results, it appeared to the author desirable that a careful re-examination of the constituents of Indian turpentine should be made, and the results so far obtained form the subject of this communication.

The oil used was distilled at the Government turpentine factory at Jallo, and was specially collected under the supervision of Mr. A. J. Gibson, Indian Forest Service, the officer in charge of the factory. It was carefully sealed up immediately after distillation in five-gallon drums, and prior to use it was dried for some days over anhydrous magnesium sulphate.

On careful fractional distillation, the presence of the following constituents was definitely proved: *l*-α-pinene, β-pinene, a new bicyclic terpene, for which the name d-*carene* is proposed, and a tricyclic sesquiterpene, *longifolene*.

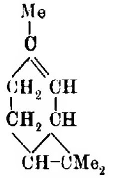
The hydrocarbon, *d*-carene, which is without doubt identical with the hydrocarbon described by Robinson (*loc. cit.*), is an oil

boiling at 168—169°/705 mm., and possessing a characteristic and curious, sweet odour. The constitution of this new terpene was determined by investigating its behaviour on treatment with hydrogen chloride and on oxidation with potassium permanganate. When treated in ethereal solution with hydrogen chloride, an oily hydrochloride was obtained, which partly solidified on cooling in a freezing mixture. The solid was found to be pure *d*-sylvestrene hydrochloride melting at 72°, whilst the terpene obtained from the liquid hydrochloride on removal of the hydrogen chloride in the usual manner (see p. 575) was found to be a mixture of sylvestrene and dipentene. The latter was identified by means of the tetrabromide after removing the greater part of the sylvestrene by treatment with potassium dichromate and sulphuric acid in the manner suggested by Baeyer (*Ber.*, 1894, **27**, 810, 3485). The formation of a mixture of sylvestrene and dipentene hydrochlorides is most simply explained if it is assumed that the new terpene is represented by one of the three following formulæ (I, II, or III),



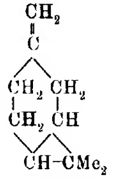
(I.)

(Δ^3-Carene.)



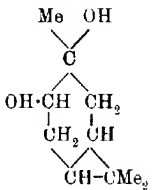
(II.)

(Δ^4-Carene.)

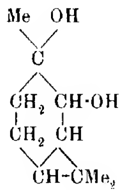


(III.)

(Dehydrocarane.)



(IV.)



(V.)

since it is obvious that a bicyclic terpene possessing one of these structures would, on fission of the *cyclo*propane ring, yield a mixture of the hydrochlorides of the monocyclic terpenes.

Further evidence in support of the above view was furnished by a study of the products formed on oxidation with potassium permanganate. When oxidised in the presence of alkali in ice-cold solution, the main product of the oxidation was found to be a *glycol*, $C_{10}H_{18}O_2$, melting at 69—70°. This glycol does not

appear to contain a primary alcohol group, since, in benzene solution, it does not react with phthalic anhydride, and it follows, therefore, that *d*-carene cannot be represented by formula III, and that the glycol must have either formula IV or V. All attempts to convert the glycol into a ketone by oxidation with chromic acid were unsuccessful, the reaction proceeding apparently abnormally with the formation of oils of high boiling point, from which nothing crystalline could be isolated. The alkaline liquid from which the glycol had been separated was acidified, and the acids formed during the oxidation carefully examined. The main product was a viscous oil, but two crystalline acids were obtained. Owing to the small yield, one of these, melting at 137°, could not be identified, but the second acid was found to be dimethylmalonic acid, thus proving definitely the presence of the grouping

$$\mathrm{CMe_2}<\begin{matrix}\dot{\mathrm{C}}\cdot\\ |\\ \underset{\cdot}{\mathrm{C}}\cdot\end{matrix}$$

in *d*-carene.

In the light of these observations, it appeared desirable to attempt to isolate caronic acid, and *d*-carene was therefore oxidised with potassium permanganate in the manner adopted by Baeyer and Ipatiev (*Ber.*, 1896, **29**, 2796) for the preparation of this acid from carone. The product of the oxidation was a viscous oil, from which nothing crystalline separated, and evidently did not contain any *cis*-caronic acid, but, on conversion into the ammonium salt, a small quantity of a crystalline salt was obtained, which was only sparingly soluble in cold water, and crystallised in glistening prisms. On acidification, an acid crystallising in prisms and melting at 212—213° was obtained, and there can be no doubt that this was *trans*-caronic acid, which is stated by Baeyer and Ipatiev to melt at this temperature (see p. 577).

So far as the author is aware, *d*-carene is the first naturally occurring terpene which has been found to contain the carane ring, and is therefore of more than usual interest. It has not been found possible to decide whether formula I or II correctly represents the structure of this terpene, and it does not appear unlikely that, as is assumed to be the case with sylvestrene, the hydrocarbon may be a mixture of the two isomerides. The molecular refraction was found to be 44·22, which agrees well with that calculated (44·19) for a compound containing a *cyclo*hexane and a *cyclo*propane ring. The fact that the molecular refraction is practically normal points to the absence of conjugation of a double bond with the *cyclo*propane ring and renders it probable that *d*-carene is represented by formula I (*d*-Δ^3-carene). It is hoped to prepare

synthetically the hydrocarbon represented by formula II (Δ^4-carene), and experiments in this direction are in progress.

The sesquiterpene for which the name *longifolene* is proposed has up to the present only been cursorily examined. It yields very beautiful derivatives with hydrogen chloride, hydrogen bromide, and hydrogen iodide, and from a consideration of its molecular refraction (M = 64·15) it is evidently tricyclic.

Experimental.

The oil used for these experiments was reddish-brown, and, after drying over magnesium sulphate, had the following constants: D_{30}^{30} 0·8717, n_D^{30} 1·4725, α_D −2·38°, acid value 2·4.

A large quantity was submitted to a careful fractional distillation under diminished pressure, using a twelve-pear Young still-head, when it was readily separated into the following three fractions: up to 118°/200 mm. (31 per cent.), 118—130°/200 mm. (47·6 per cent.), 149—155°/36 mm. (10·2 per cent.); loss and residue (by difference), 11·2 per cent.

The fractions boiling below 130°/200 mm. were carefully refractionated under the ordinary pressure, and were divided into two main fractions, *A* distilling at 155—167°/706 mm. (60·8 per cent.) and *B* at 167—171°/706 mm. (14·8 per cent.). Fraction *A* consisted mainly of α- and β-pinene, and a pure fraction of *l* α pinene was isolated boiling at 153—154°/700 mm. and possessing the following constants: D_{27}^{27} 0·8525, n_D^{28} 1·4625, α_D −34°, which agree well with those usually found for this hydrocarbon. The identity was further confirmed by the formation of α-pinonic acid on treatment with potassium permanganate in the usual manner. The presence in fraction *A* of β-pinene was proved by the isolation of nopinic acid (m. p. 128°) from the products of the oxidation with potassium permanganate in the usual manner.

d-*Carene* (d-Δ^3- *or* -Δ^4-*Carene*).

The fraction *B* (see above) was found on repeated fractionation to yield an oil, which boiled quite constantly at 168–169°/705 mm., 123—124°/200 mm. This hydrocarbon, for which the name *d*-carene is proposed, was found to have the following constants: D_{30}^{30} 0·8586, n_{30} 1·469, α_D +7·69°. M = 44·23, calc. for $C_{10}H_{16}|\overline{=}$ = 43·5, which, with the increment for the presence of a *cyclo*propane ring (0·69), becomes 44·19 (compare Eisenlohr, "Spektrochemie der organischen Verbindungen," p. 131).

Another sample of *d*-carene from a different sample of turpen-

tine was found to have the following constants: D^{27}_{27} 0·8591, n^{27}_{D} 1·47, α_D +7·83°.

Owing to the readiness with which *d*-carene is oxidised on exposure to the air, only approximate figures were obtained on analysis. A specimen distilled three times over sodium under diminished pressure and analysed immediately gave the following figures:

0·1019 gave 0·327 CO_2 and 0·107 H_2O. C=87·5; H=11·7.
$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

d-Carene is a colourless oil possessing a very characteristic, somewhat sweet odour. When dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, a transient, green coloration was observed. Unlike sylvestrene and terpinene, it was found not to be acted on by a mixture of potassium dichromate and sulphuric acid. The ease with which it undergoes oxidation was shown by the fact that when 1 c.c. was placed in a closed vessel, it absorbed all the oxygen present in three days.

In chloroform solution, *d*-carene readily absorbed bromine, but after the addition of one molecular proportion, the absorption became very slow and hydrogen bromide commenced to be evolved. It was not found possible to obtain a solid bromo-derivative, whilst the nitrosochloride and the nitrosite could also only be obtained as oils; it yielded, however, a crystalline *nitrosate*. The terpene (5 grams) was mixed with acetic acid (2 c.c.) and amyl nitrite (4 grams), and nitric acid (D 1·4) (3·5 grams) was then added very slowly to the well-cooled mixture. A solid was slowly deposited, and, after an hour, alcohol was added and the solid collected. It was purified by crystallisation from a mixture of chloroform and light petroleum, when it was obtained in glistening prisms which decomposed at 141·5°:

*0·089 gave 11 c.c. N_2 at 34° and 741 mm. N=12·8.
$C_{10}H_{16}O_3N_2$ requires N=13·2 per cent.

d-*Carene nitrosate* is very sparingly soluble in methyl and ethyl alcohols or light petroleum, more readily so in acetone or chloroform.

d-Carene showed no tendency to undergo hydration when treated with dilute sulphuric acid. In one experiment, the terpene (20 grams) was heated at 100° for seven days with dilute sulphuric acid (5 per cent.) (100 c.c.) in a closed vessel from which the air had been displaced by carbon dioxide. The terpene distilled completely at 123—124°/200 mm., and that it was quite unaffected

* I wish to thank Prof. B. K. Singh for this analysis.

by the treatment is indicated by the following constants: D_{25}^{25} 0·8595, n_D^{28} 1·469.

Action of Hydrogen Chloride on d-*Carene.*

As has already been mentioned, *d*-carene on treatment with hydrogen chloride gives a mixture of *d*-sylvestrene and dipentene hydrochlorides. In one experiment, the terpene (30 grams) was dissolved in dry ether (60 c.c.), and dry hydrogen chloride passed into the well-cooled solution until it was saturated. After two days, the ether was removed in a vacuum, and the residual brown oil cooled in a freezing mixture, when it partly solidified. The crystals were rapidly collected, and, after draining on porous porcelain, were found to melt at 71° (yield, 6 grams). On recrystallisation from methyl alcohol, the hydrochloride separated in glistening needles melting at 72°, and evidently consisted of sylvestrene hydrochloride. In chloroform solution, $[\alpha]_D$ had the value +20·31° (Found: Cl=33·7. $C_{10}H_{18}Cl_2$ requires Cl=33·9 per cent.). A quantity of the hydrochloride was converted into the terpene, which was found to possess all the properties ascribed to *d*-sylvestrene.

The liquid hydrochloride (40 grams) from which the *d*-sylvestrene hydrochloride had been separated was mixed with acetic acid (80 grams) and sodium acetate (40 grams) and heated for thirty minutes on the sand-bath. The hydrocarbon was distilled in a current of steam, separated, and, after boiling for a short time with potassium hydroxide solution, extracted with ether, the ether dried and evaporated, and the residual oil distilled at 200 mm., when 12 grams of an oil were obtained distilling between 120° and 140°. The hydrocarbon, which had a pleasant odour of lemons, gave, when dissolved in acetic acid, an intense sylvestrene coloration with sulphuric acid. In order to remove the greater portion of the sylvestrene, the mixture of terpenes was repeatedly shaken (twenty times) with small quantities of dilute potassium dichromate solution (compare Baeyer, *loc. cit.*). After drying over potassium carbonate, the remaining oil was distilled over sodium, when the greater portion passed over at about 130°/200 mm. (yield, 5 grams). The terpene, which still gave the sylvestrene reaction, although much less markedly than before, was dissolved in chloroform and treated with a chloroform solution of bromine until a permanent straw coloration was obtained, the chloroform removed in a vacuum, and the residual viscid oil cooled in a freezing mixture, when it rapidly crystallised. After draining on porous porcelain, the bromo-derivative was purified by crystallisation from ethyl acetate, when it was found to melt at

123—124°, and this melting point was not depressed on admixture with a specimen of dipentene tetrabromide from another source (Found: Br = 70·6. $C_{10}H_{16}Br_4$ requires Br = 70·2 per cent.).

Oxidation of d-*Carene: I.* d-*Carene Glycol* (IV *or* V).

The terpene (50 grams) was mixed with sodium hydroxide solution (500 c.c.; 50 grams of NaOH), and, after the addition of ice, potassium permanganate solution (1·5 litres; 116 grams of $KMnO_4$) was gradually added with constant shaking, the solution being kept at 0° during the addition. The oxidation, which proceeded rapidly at first, became very slow towards the end. When the colour of the potassium permanganate had disappeared, steam was passed into the solution to remove the unchanged terpene (20 grams), the solution filtered, and concentrated on the water-bath, carbon dioxide being passed into the liquid during evaporation. The alkaline solution was extracted ten times with ether to remove the neutral products formed during the oxidation, the ethereal extract dried over potassium carbonate, the ether evaporated, and the residual oil distilled under diminished pressure, when practically the whole passed over at 166—167°/42 mm. On keeping, the viscous oil rapidly crystallised in long needles melting at 69—70°:

0·1402 gave 0·361 CO_2 and 0·131 H_2O. C = 70·2; H = 10·4.

$C_{10}H_{18}O_2$ requires C = 70·6; H = 10·6 per cent.

d-*Carene glycol* is readily soluble in all the ordinary organic solvents, and it was not found possible to recrystallise it. In chloroform solution it has $[\alpha]_D$ + 16·05. *d*-Carene glycol does not react with phthalic anhydride when heated in benzene solution on the water-bath, and it is therefore extremely unlikely that it contains a primary alcohol group. When mixed with sulphuric acid (D 1·25) it readily dissolved, and on keeping a viscid oil separated which could not, however, be obtained crystalline. It reacted readily with hydrogen bromide, but the product could not be obtained solid. In acetic acid solution it was oxidised by chromic acid with the formation apparently of a complex mixture, from which, owing to the small quantity of material at the author's disposal, nothing definite could be isolated.

The alkaline liquid from which the glycol had been separated was acidified with dilute sulphuric acid and repeatedly extracted with ether. On removal of the ether a viscid oil remained which had a strong odour of butyric acid. As the oil showed no tendency to crystallise it was esterified in the usual manner with alcohol and sulphuric acid, and the resulting mixture of esters carefully frac-

tionated under diminished pressure (44 mm.). A small quantity distilled below 160°, and three main fractions were collected: *A* at 160—170°, *B* at 170—185°, and *C* at 180—200°.

Fraction *A*, which was a pleasant-smelling oil, was hydrolysed with alcoholic potassium hydroxide solution in the usual manner, and after removal of the alcohol and acidification the aqueous solution was repeatedly extracted with washed ether, the ethereal extract dried and evaporated, when an oil was obtained which rapidly solidified. After draining on porous porcelain, the acid was recrystallised from water, when it separated in small plates which decomposed at 186—187° and evidently consisted of dimethylmalonic acid (Found, C=45·2; H=5·8. $C_5H_8O_4$ requires C=45·4; H=6·1 per cent.).

The view that this acid was dimethylmalonic acid was confirmed by the fact that when mixed with a specimen of dimethylmalonic acid from another source no depression of the decomposition point was observed.

Fraction *B*, which was a somewhat viscous, unpleasant-smelling oil, was hydrolysed with alcoholic potassium hydroxide solution, and the acid obtained in this way was isolated by extraction with ether in the usual manner. The acid was a very viscous, unpleasant-smelling oil, which on trituration with a little water partly solidified. The solid was separated, drained on porous porcelain, and purified by crystallisation from dilute methyl alcohol, when it crystallised in long, prismatic needles melting at 136—137°. On analysis it gave the following figures:

0·1349 gave 0·3537 CO_2 and 0·1008 H_2O. C=71·5; H=8·3.

This result agrees best with the formula $C_{10}H_{14}O_2$ (C=72·3; H=8·4 per cent.), but owing to the very poor yield of this acid it was not found possible to determine its constitution.

Fraction *C* on hydrolysis gave a viscous oil smelling strongly of fatty acids. It could not be obtained crystalline, and was not further investigated.

II. trans-*Caronic Acid.*

The method adopted for the preparation of *trans*-caronic acid from *d*-carene was identical with that used by Baeyer and Ipatiev (*loc. cit.*) for the preparation of this acid from carone. The oily mixture of acids obtained from the oxidation (no trace of the *cis*-acid could be detected) was converted into the ammonium salt when after concentration the ammonium hydrogen salt of *trans*-caronic acid separated. This was recrystallised from a little water, in which it was only sparingly soluble when it was obtained in small

prisms. The free acid was purified by crystallisation from hot water, when it separated in prisms melting at 212—213°. This acid possessed all the properties ascribed to *trans*-caronic acid, and the melting point was not depressed on admixture with a specimen of *trans*-caronic acid specially prepared for comparison.

The silver salt was obtained as a crystalline precipitate (Found, Ag=57·7. $C_7H_8O_4Ag_2$ requires Ag=58·1 per cent.).

d-*Longifolene.*

The fraction of the original oil boiling at 149—151°/36 mm. was repeatedly distilled over sodium, when the sesquiterpene d-*longifolene* was obtained as a colourless, somewhat viscous oil with a faint and not unpleasant odour. It distilled at 254—256°/706 mm., 150—151°/36 mm., and had the following constants: D_{30}^{30} 0·9284, n_D^{30} 1·495, M=64·15, α_D +42·73°.

d-Longifolene does not yield a solid nitrosochloride, nitrosate, or nitrosite.

The *hydrochloride* was best prepared by saturating an ethereal solution of the hydrocarbon with hydrogen chloride and allowing it to remain overnight. On removing the ether under diminished pressure, the hydrochloride separated as a crystalline solid which crystallised from methyl alcohol in long prisms or prismatic needles melting at 59—60° and having, in chloroform solution, $[\alpha]_D$ +7·1°:

0·1866 gave 0·1109 AgCl. Cl=14·7.

$C_{15}H_{25}Cl$ requires Cl=14·7 per cent.

The *hydrobromide* was best prepared by dissolving the terpene in an acetic acid solution of hydrogen bromide (saturated at 0°) when, on keeping, the hydrobromide separated in prisms which after crystallisation from alcohol melted at 69—70°:

0·1672 gave 0·111 AgBr. Br=28·2.

$C_{15}H_{25}Br$ requires Br=28·0 per cent.

The *hydriodide* which was prepared in a similar manner to the hydrobromide crystallised from alcohol in magnificent prismatic needles which melted at 71°:

0·119 gave 0·0838 AgI. I=38·2.

$C_{15}H_{25}I$ requires I=38·0 per cent.

In conclusion, the author wishes to thank his assistant, Mr. T. P. Ghose, for help in the experimental work, and Mr. M. Gopal Rau for many of the analyses and for kindly undertaking the preparation of the dimethylmalonic acid and *trans*-caronic acid required for the purpose of comparison.

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[*Received, April 8th,* 1920.]

LXII.—*The Cyanine Dyes. Part I. The Constitution of the* iso*Cyanines.*

By William Hobson Mills and Robert Scott Wishart.

The *iso*cyanines were discovered in 1883 by Spalteholz (*Ber.*, 1883, **16**, 1847), and independently by Hoogewerff and van Dorp (*Rec. trav. chim.*, 1883, **2**, 41; 1884, **3**, 344). These investigators found that a purplish-red dye forming magnificent, lustrous green crystals could be obtained from a mixture of the ethiodides of quinaldine and quinoline by the action of potassium hydroxide. Hoogewerff and van Dorp assigned to it the formula $C_{23}H_{23}N_2I$—that is to say, they regarded it as formed by the condensation of one molecule of quinaldine ethiodide with one of quinoline ethiodide with the elimination of hydrogen iodide and of two atoms of hydrogen,

$$C_{12}H_{14}NI + C_{11}H_{12}NI = C_{23}H_{23}N_2I + HI + 2H.$$

Since the compound thus corresponded in composition as well as in general properties with the well known blue dye cyanine, discovered by Greville Williams, similarly formed from the alkyl-iodides of lepidine and quinoline, Hoogewerff and van Dorp named it diethyl*iso*cyanine iodide. Spalteholz formulated the dye as $C_{23}H_{25}N_2I$.

Interest was again aroused in the *iso*cyanines when their value as photographic sensitisers became recognised (Miethe and Traube, *Chem. Ind.*, 1903, **26**, 54).

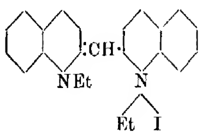
The first suggestion as to the constitution of this class of dyes was made by Decker (*Ber.*, 1891, **24**, 692). Having discovered the alkylquinolinium pseudo-bases (*loc. cit.* and *Ber.*, 1892, **25**, 3326), he saw in them the reactive intermediate products to which the formation of the dyes of the cyanine type was due, and accordingly he expressed the view that the cyanines were the product of the interaction of one molecule of unchanged alkyl-iodide with one molecule of 1-alkyl-2-quinolone arising from the oxidation of the pseudo-base. The idea that the quinolinium pseudo-bases play a principal part in the production of these dyes forms the basis of all the formulæ which have been proposed for the *iso*cyanines.

Another point on which there has been general agreement is that the 2-methyl group of the quinaldine alkyl-iodide is concerned in the condensation. This question has been dealt with especially by Vongerichten and Höfchen (*Ber.*, 1908, **41**, 3054). These investigators showed in the first place that quinaldine alkyl-iodides in which the hydrogen atoms of this methyl group are substituted, as benzylidenequinaldine ethiodide or 2-*iso*propylquinoline meth-

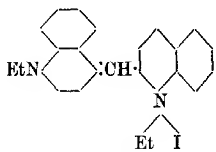
iodide, are incapable of taking part in the formation of *iso*cyanines. It should, however, be pointed out that evidence of this nature, which has been used to a considerable extent in the discussion of the constitution of these dyes, is not altogether conclusive, since the *iso*cyanine condensation is very subject to steric hindrance. Quinoline alkyl-iodides, for example, are prevented from taking part in this condensation by substitution, not only in the 4-position (Miethe and Book, *Ber.*, 1904, **37**, 2823; Kaufmann and Vonderwahl, *Ber.*, 1912, **45**, 1404), but also as experiments of Miss F. M. Hamer and Mr. W. K. Braunholtz in this laboratory have shown, in the 5-position, and, according to the patent literature, in the 8-position.

Vongerichten and Höfchen (*loc. cit.*) also showed that 1-ethyl-2-quinolone is formed when diethyl*iso*cyanine chloride is oxidised with alkaline potassium ferricyanide. This proves that the nucleus of the quinaldine residue is linked to the rest of the *iso*cyanine molecule through the 2-position, and therefore presumably through the carbon atom of the 2-methyl group.

On the assumption that the *iso*cyanines are formed by condensation, through the 2-methyl group, of a quinaldine alkyl-iodide with a quinolinium pseudo-base, with or without concomitant oxidation, the three following formulæ have been proposed for diethyl*iso*cyanine iodide:



(I.)



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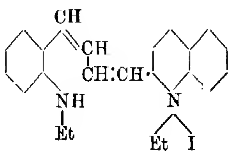


(III.)

The first of these is Decker's formula (*J. pr. Chem.*, 1911, [ii], **84**, 235). It follows at once from Decker's view of the mechanism of the *iso*cyanine condensation. The second formula was suggested by W. König (*J. pr. Chem.*, 1906, [ii], **73**, 100) as a modification, which he regarded on general grounds as more probable, of a formula proposed by Miethe and Book (*Ber.*, 1904, **37**, 2008). It differs from Decker's formula in that it represents the quinoline

residue as linked to the rest of the molecule through the 4′- instead of the 2′-position. Very strong evidence that the quinoline residue is actually linked through the 4′-position was obtained by A. Kaufmann and Vonderwahl (*Ber.*, 1912, **45**, 1404). In particular, they showed that quinoline alkyl-iodides substituted with chlorine in the 4-position reacted with quinaldine ethiodide and alkali, with the elimination of hydrogen chloride as well as of hydrogen iodide, to give the same *iso*cyanines as are formed from the corresponding chlorine-free compounds. Their important communication thus affords strong support to König's formula (II). The third formula was also proposed by König. It is based on the view that the pseudo-bases derived from quinoline alkyl-iodides are aldehyde-amines, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CHO$, and represents the *iso*cyanines as the normal condensation products of these with quinaldine alkyl iodides. This interesting suggestion which, although it had little direct experimental support, could scarcely be proved to be at variance with the facts, will be further considered in a later paper.

Whilst the available evidence must thus be regarded as favouring the second of these three formulæ, it was not of a very direct character, and further information which would assist in furnishing a more secure basis for a constitutional formula for the *iso*cyanines was desirable.

Certain observations had led us to believe that the investigation of the action of potassium permanganate on these dyes would lead to results of interest. We have therefore studied the oxidation by this reagent of 1:1-dimethyl*iso*cyanine acetate (the dimethyl compound was selected as being the simplest *iso*cyanine and the acetate because it was the most readily soluble of its salts with common acids), and in the present communication an account is given of the results we have obtained.

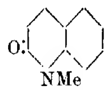
As has already been stated, the oxidation of an *iso*cyanine has previously been investigated by Vongerichten and Höfchen (*loc. cit.*). These authors, using alkaline potassium ferricyanide, isolated a 1-alkylquinolone, and showed that it was derived from the quinaldine half of the molecule, but they were unable to isolate the other products of oxidation.

The oxidation of dimethyl*iso*cyanine acetate with potassium permanganate proceeds very smoothly in ice-cold aqueous solution, and the end of the reaction is sharply marked by the point at which the colour of the gradually added permanganate persists. The quantity of permanganate used corresponds with approximately $3\frac{1}{2}$ atoms of oxygen for one molecule of *iso*cyanine.

From the oxidised solution we were able to isolate 1-methyl-2-quinolone (IV) and, after acidification with hydrochloric acid,

cinchonic acid methochloride (V). (The actual product of the oxidation was probably the corresponding betaine.) The weights of these products, before purification, amounted to approximately 80 and 70 per cent. respectively of those theoretically possible. These two

(V.)

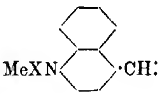


(IV.)

compounds account for all the carbon atoms in the *iso*cyanine, and the two molecules together contain 3 atoms of oxygen. It is clear, therefore, that 3 atoms of oxygen are required for the oxidation, the half atom or so actually used in excess of this quantity being consumed in side reactions. Hence the equation for the reaction is:

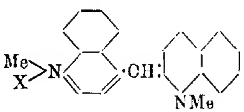
$$C_{21}H_{19}O_3N_2X + 3O = C_{10}H_9ON + C_{11}H_{10}O_2NX.$$

The composition of the products and the number of oxygen atoms used in their formation thus settle the debated question of the number of hydrogen atoms in the molecule of the *iso*cyanine; they show that the view of Hoogewerff and van Dorp that the condensation involves the removal of two atoms of hydrogen by oxidation is correct. At the same time the structural formula of the dye is fixed. For subtraction of the added oxygen atoms from the two products leaves the residues

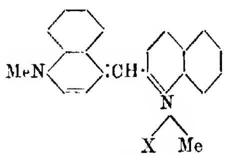


and

and these on combination give VI as the formula of the *iso*cyanine.



(VI.)



(VII.)

This formula stands in the closest relationship to formula II suggested by König and advocated by Kaufmann and Vonderwahl. In fact, since in each the two nitrogen atoms are connected by a chain of conjugate linkings, it is probable that the two types of formulæ represent virtually tautomeric compounds.

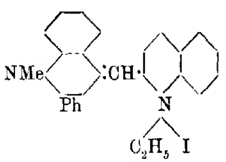
If this should prove to be the case, the objection might perhaps be raised that, whilst the experiments recorded in this paper show

definitely that the dimethyl*iso*cyanine salts have one of the (supposedly) tautomeric formulæ, VI or VII, they do not provide a satisfactory basis for distinguishing between these two. It might be argued that the compound actually oxidised was the *iso*cyanine base set free by the excess of alkali developed by the reduction of the permanganate, especially as the salt employed was that of a weak acid, and that the base might differ in constitution from the salts. The nature of the oxidation products, however, shows that, if they are derived from a base, this must be an ammonium base, not a pseudo-base; and a strong quaternary ammonium base, as this must be, must correspond in constitution with its salts. For if the compounds are tautomeric, as supposed, the acid radicle of the salt and the hydroxyl group of the base must each be attached to the more strongly basic of the two nitrogen atoms.

There is further no apparent reason why a compound of the formula VII, if present, should not be about as readily oxidised to 1-methyl-4-quinolone and a 1-methylquinaldinic acid salt as the substance VI is oxidised to 1-methyl-2-quinolone and a 1-methylcinchonic acid salt. An experiment was carried out in which the quantity of acetic acid necessary to keep the reaction mixture neutral was added to the permanganate solution before it was allowed to run into the *iso*cyanine. The products of oxidation were the same as in weakly alkaline solution and, in spite of careful search, no evidence of the formation of 1-methyl-4-quinolone or of a 1-methyl quaternary salt of quinaldinic acid could be obtained.

It would therefore appear justifiable to draw from these experiments the inference that the dimethyl*iso*cyanine salts have the structure represented by formula VI.

There is an observation of Kaufmann and Vonderwahl which confirms this suggestion of the virtual tautomerism of the *iso*cyanines. These authors have shown (*Ber.*, 1912, **45**, 1418) that 1-ethyl-1'-methyl-2'-phenyl*iso*cyanine iodide (VIII), when heated in a high



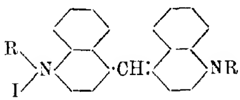
(VIII.)

vacuum, decomposes into ethyl iodide and a base having the composition of a phenylmethylquinolylene-quinaldine. This proves that in this compound the iodine is attached to the nitrogen atom in the quinaldine residue, otherwise methyl iodide would be eliminated.

This substance therefore has the formula VIII, and does not correspond in constitution with the dimethyl*iso*cyanine salts. It is noteworthy that, like other 2′-substituted *iso*cyanines, it is an exceedingly feeble sensitiser (Pope and Mills, *Phot. J.*, 1920, **60**).

If, as would thus appear, the *iso*cyanines are virtually tautomeric compounds, differences of constitution of this kind would be expected to occur. In the compound VIII the basicity of the nitrogen in the quinoline residue must be lowered by the presence of the adjacent phenyl group, and it is probable that a reversal is thereby brought about of the normal order of basicity of the two nitrogen atoms which obtains in the simpler *iso*cyanines. Thus, whilst the powerfully sensitising 1:1′-dimethyl*iso*cyanine salts, and therefore presumably also the closely related 1:1′-diethyl- and 1:1′:6-trimethyl-*iso*cyanine salts have molecular constitutions corresponding with formula VI, certain *iso*cyanines negatively substituted in the quinoline half of the molecule must be regarded as having a structure of the type represented by **VII**.

The cyanines correspond so closely with the *iso*cyanines in formation, composition, and general properties that it has been generally recognised that their constitution must follow from that of the latter class of dyes. The formula VI established for the *iso*cyanines therefore practically fixes that of the cyanines as



EXPERIMENTAL.

Oxidation of 1:1′-*Dimethyl*iso*cyanine Acetate.*

Since it was desirable to carry out the oxidation of the *iso*cyanine in aqueous solution, and the chloride, nitrate, and sulphate of the dye were found to be sparingly soluble in water, the more readily soluble acetate was prepared by treating the iodide with silver acetate. 1:1′-Dimethyl*iso*cyanine iodide (Pope and Mills, *loc. cit.*) (5 grams) was dissolved in alcohol (250 c.c.), silver acetate (10 grams) ground into a cream with alcohol (30 c.c.) was added, and the mixture was boiled for half an hour. The solution, which was then found to be free from iodide, was filtered, and the filtrate was evaporated to dryness, the last traces of alcohol being carefully removed by a current of warm air. The dimethyl*iso*cyanine acetate obtained in this way was dissolved in water (250 c.c.), and this solution was used for the oxidation. It was browner than true

solutions of dimethyl*iso*cyanine salts, and was possibly a colloidal solution, since the addition of a little acetone immediately restored the brilliant *iso*cyanine colour, and dilution with water had the same effect.

To carry out the oxidation the aqueous solution of the acetate was cooled to 0° and a 3 per cent. solution of potassium permanganate was allowed to drop slowly into the rapidly stirred liquid until a drop placed on filter paper showed the first signs of a permanganate-coloured ring round the moistened spot. In an experiment in which the acetate from 1·74 grams of iodide was dissolved in 100 c.c. of water and oxidised in this manner, 45·7 c.c. of 3 per cent. potassium permanganate solution were required. Since the molecular weight of the iodide, which contains one molecule of methyl alcohol of crystallisation, is 458, the permanganate used corresponds with 3·42 atoms of oxygen per molecule of *iso*cyanine. In most of our later experiments the acetate solution prepared from 5 grams of iodide was divided into two equal parts, and to each of these 67·5 c.c. of a 3 per cent. potassium permanganate solution, corresponding with 3·55 atoms of oxygen per molecule of *iso*cyanine, was added.

Isolation of 1-*Methyl*-2-*quinoline*.—After the addition of the permanganate solution was complete, the precipitated manganese dioxide was removed, and the pale brown filtrate was extracted with chloroform. The chloroform solution, after being dried with potassium carbonate, was evaporated; the brown residue, placed in a vacuum desiccator over solid paraffin and sulphuric acid, became solid after some days. Extraction of the residue with light petroleum (b. p. 40—60°) gave a pale yellow solution, which, on cooling, deposited a substance crystallising in long, colourless needles. After recrystallisation from light petroleum, this substance melted at 73—74°, which is the melting point of 1-methyl-2-quinolone (Knorr and Rabe, *Ber.*, 1897, **30**, 930). The analytical results agreed with those required for this compound. (Found, C=75·75; H=5·7. $C_{10}H_9ON$ requires C=75·43; H=5·7 per cent.)

The hydrochloride obtained by treating the quinolone with hydrochloric acid melted at 110—113° and the mercurichloride at 189°. The melting points recorded for these compounds are 112° and 189° (Ostermayer, *Ber.*, 1885, **18**, 595; Friedländer and Müller, *Ber.*, 1887, **20**, 2010).

A specimen of 1-methyl-2-quinolone was then prepared from quinoline methiodide by oxidation with alkaline potassium ferricyanide as described by Decker (*J. pr. Chem.*, 1893, [ii], **47**, 31), and a comparison of this with the compound obtained from the *iso*cyanine and, in particular, the agreement of the mixed melting points of the bases, the hydrochlorides, and the mercurichlorides with those of

the separate substances left no doubt as to the identity of the two compounds. From 5 grams of dimethyl*iso*cyanine iodide 1·38 grams of crude methylquinolone were obtained. This weight is 79—80 per cent. of the theoretical amount.

Isolation of Cinchonic Acid Methochloride.—After the removal of the methylquinolone by extraction with chloroform the weakly alkaline liquid was acidified with hydrochloric acid and boiled for an hour with animal charcoal (5 grams). The nearly colourless filtrate from the charcoal was then evaporated to dryness and the residue extracted with absolute alcohol. The alcoholic extract having been concentrated to a volume of about 7 c.c., two volumes of ether were gradually added, when a flocculent precipitate of cinchonic acid methochloride was formed, which was collected and dried; 1·7 grams were thus obtained from 5 grams of dimethyl*iso*cyanine iodide, a weight which corresponds with 69—70 per cent. of the theoretical amount.

As cinchonic acid methochloride is too soluble to be readily recrystallised, it was converted into the corresponding methiodide and methylbetaine, and the identification of these compounds was effected in the following manner.

Cinchonic Acid Methiodide.—This substance was obtained by adding 1 c.c. of a saturated solution of potassium iodide to a concentrated aqueous solution of the chloride (1·5 grams) slightly acidified with hydrochloric acid. The yellow, crystalline precipitate crystallised from alcohol in fine yellow needles melting at 222°, which is the melting point of cinchonic acid methiodide (H. Meyer, *Monatsh.*, 1903, **24**, 201). A specimen of cinchonic acid methiodide (*b*) was prepared from cinchonic acid as described by H. Meyer (*loc. cit.*), and the synthesised compound was carefully compared with that obtained from dimethyl*iso*cyanine iodide (*a*). Both substances, as well as a mixture of the two, melted at 222°, and both, air-dried under the same conditions, contained practically the same percentage of iodine. (Found, I=(*a*) 37·0, (*b*) 37·3. $C_{11}H_{10}O_2NI,H_2O$ requires I=38·1 per cent.)

After drying at 110° and 10 mm.: Found, (*a*) C=41·5, H=3·5; (*b*) C=41·5, H=3·4. $C_{11}H_{10}O_2NI$ requires C=41·9; H=3·2 per cent.

Cinchonic Acid Methylbetaine.—The methiodide was converted into the corresponding betaine in the usual manner by treating it in aqueous solution with silver oxide and evaporating the filtrate to dryness over sulphuric acid in a vacuum. The betaine was purified by dissolving in absolute alcohol and precipitating with dry ether, and then formed colourless needles melting and decomposing at

219—221° (*a*). A specimen of cinchonic acid methylbetaine, prepared in exactly the same manner from the synthetic methiodide, melted and decomposed at 222—223° (*b*), and the mixture of the two substances melted at the same temperature. Also close correspondence was shown in the behaviour of the two substances when heated side by side in the same bath, darkening beginning in each case at 170°. Claus (*Annalen*, 1892, **270**, 347) gives the melting point of this compound, which varies somewhat with the rate of heating, as 236° (decomp.), and H. Meyer (*loc. cit.*) as 232° (decomp.). Both specimens of betaine were analysed. (Found, (*a*) C=70·4; H=4·8; (*b*) C=70·6; H=4·85; $C_{11}H_9O_2N$ requires C=70·6; H=4·8 per cent.).

When aqueous solutions of the betaine and picric acid are mixed a picrate is formed, crystallising in long, yellow needles. Specimens of this picrate prepared from the betaine from the *iso*cyanine and from the synthetic betaine both melted at 228°, and the melting point of a mixture showed no depression.

The alcohol–ether solution from which the cinchonic acid methochloride had been precipitated contained a small quantity of another chloride melting at 193—194° and giving a picrate melting at 159—161°. Insufficient of this substance was obtained to allow of its identification. It is, however, quite different from quinaldinic acid methochloride.

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LXIII.—*Experiments on the Preparation of Oximino-derivatives.*

By WILLIAM KERSHAW SLATER.

THE conversion of ketones into oximino-derivatives by the action of alkyl nitrites and mineral acids, in accordance with the general equation

$$R\cdot CO\cdot CH_2\cdot R' + Alk\cdot O\cdot NO = R\cdot CO\cdot C(:NOH)\cdot R' + Alk\cdot OH,$$

appears to have been first carried out almost simultaneously by Claisen (*Ber.*, 1887, **20**, 252) and Sandmeyer (*ibid.*, 639). The method has since been extended to a large variety of ketones, but has proved to be by no means generally applicable.

There is little in the work hitherto published on the subject

which serves to explain the variable yields obtained in different cases, or to make possible a reasonable forecast of the approximate conditions likely to ensure even a partial success in applying the method to a new ketone.

Researches, on which the present author and others have been engaged for some time in these laboratories, have emphasised these defects in our very empirical knowledge of the reaction in question.

Prof. Lapworth suggested that a comparative study of ketones of several different types should be undertaken, special attention being devoted to the influence of the mineral acid catalyst, the nature, concentration, and condition of which were evidently the most important factors in determining the course of the reaction and the yields obtained. The activity of the catalyst is determined by many factors, and not least by the basic character of the solvent. Variations in the activity of the catalyst might have been avoided by working in aqueous solution, but, owing to the well-known depressant effect of water on the catalytic activity of hydrogen chloride, the quantity of catalyst required under these conditions is inconveniently large. In the less basic solvent, ether, the quantity of hydrogen chloride required is very small, but its activity is seriously influenced by traces of water.

Ether has, however, a further advantage in that it can be easily removed from the products, and, in consequence of this property, was adopted as the solvent. The alkyl nitrite employed was methyl nitrite, which the author some years ago had used with considerable success in unpublished researches carried out in conjunction with Prof. Lapworth.

Preparation of Methyl Nitrite.

The methyl nitrite was prepared by dropping sulphuric acid (one part of acid to two of water) on a mixture of methyl alcohol and sodium nitrite in molecular proportions, diluted with its own volume of water. The mixture was heated on a water-bath and the vapour passed through a reflux condenser to retain the methyl alcohol. The methyl nitrite was then passed through a cooled U-tube containing glass wool, and finally through a calcium chloride tube before it entered the absorption apparatus, which consisted of a gas jar fitted with a rubber stopper carrying a short, efficient condenser, a Witt stirrer sealed with light petroleum oil, and two lead tubes, one for methyl nitrite and the other for hydrogen chloride.

Method of carrying out the Reaction.

The ketone under investigation, dissolved in five times its own bulk of ether, was placed in the reaction vessel, the stirrer started, and about 10 c.c. of hydrogen chloride were introduced. The stream of methyl nitrite was allowed to enter, and absorption took place rapidly, the ethereal solution being drawn up the delivery tube if the stream of gas was not maintained constant.

It was found that in order to carry on the reaction, 10 c.c. of hydrogen chloride had to be added every fifteen minutes. This addition appeared to correspond with the rate at which the catalyst was used up.

The reaction was continued until the solution would absorb no more methyl nitrite, which in the average case required from one and a-half to two hours. The oximino-derivative was obtained by evaporating off the ether either in a stream of dry air or by gently heating on the water-bath. The subsequent treatment of the material depends on the individual ketone under investigation.

The reaction was studied for four general classes of ketones.

(1) Aryl$\cdot$CO$\cdot$$CH_3$. Example, acetophenone.
(2) Alkyl$\cdot$CO$\cdot$$CH_3$. Example, acetone.
(3) Alkyl$\cdot$CO$\cdot$$CH_2$$\cdot$$CH_3$. Example, methyl ethyl ketone.
(4) Aryl$\cdot$CO$\cdot$$CH_2$$\cdot$$CH_3$. Example, propiophenone.

Oximinoacetophenone and Oximinoacetone.

In a considerable number of uniform experiments, 10 grams of acetophenone gave, on evaporating methyl alcohol and ether, 11 grams of oil, and this, after agitation with 10 per cent. sodium hydroxide and ether, was divided into 5·1 grams of unchanged ketone and 4·2 grams of oximinoacetophenone, corresponding with a conversion of about 40 per cent. Halving the concentration of hydrogen chloride led to a 20 per cent. yield, whilst doubling it not only failed to raise the yield above 40 per cent., but led to an increased production of by-products, amongst which is a lachrymatory material. Furthermore, experiments with mixtures of the ketone and its oximino-derivative showed that with a constant concentration of the catalyst, action would not proceed after the above maximum had occurred.

The case of acetone exactly resembled that of acetophenone, 6 grams of the oximino-derivative being obtained; the method is not so satisfactory as that of Tschugaev (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466), depending on acetoacetic ester.

Oximinomethyl Ethyl Ketone and Oximinopropiophenone.

These substances represent the second type of compound, in which the reaction proceeds almost to completion. Ten grams of methyl ethyl ketone yielded 13·6 grams of the oximino-derivative, corresponding with a 97 per cent. yield. This oximino-derivative appeared to be much less sensitive to the hydrogen chloride than those previously described.

The case of propiophenone resembled that of methyl ethyl ketone, but the yields were not so satisfactory, owing to the formation of what the author believes to be the corresponding nitroso derivative. Five grams of propiophenone yielded 6 grams of oil which, on treatment with 10 per cent. sodium hydroxide and ether, gave a bright bluish-green, ethereal solution. This solution was shaken with anhydrous sodium carbonate, and yielded 4·5 grams of oximinopropiophenone, which corresponds with 75 per cent. of the theoretical.

Ethyl Oximinoacetoacetate.

The application of the method to acetoacetic ester resulted in the formation of the *syn*-oximino-derivative described by Jovitschitsch (*Ber.*, 1895, **28**, 2685).

Five grams of acetoacetic ester yield 6 grams of an oil which consisted almost entirely of ethyl oximinoacetoacetate.

Summary of Results.

As the result of the investigation, it is possible to divide ketones into two general classes, namely, (1) those containing the grouping $R{\cdot}CO{\cdot}CH_3$, and (2) those containing the grouping

$$R{\cdot}CO{\cdot}CH_2{\cdot}CH_3.$$

The oximino-derivatives of the first class appear to be very sensitive to hydrogen chloride, and, consequently, it is advisable in dealing with ketones of this class to reduce the concentration of the catalyst to a minimum.

The oximino-compounds of the second class are much more stable towards hydrogen chloride, and the concentration of the catalyst can be varied between wide limits without materially influencing the end-product.

It is hoped that these observations may serve as a guide when details for the preparation of an unknown oximino-derivative are required.

ADDENDUM.

The Preparation of Cupferron.

The use of methyl nitrite was tried in the preparation of ɪpferron (ammonium salt of *N*-nitroso-β-phenylhydroxylamine), ɪd was attended by excellent results, as the following example ill indicate.

Ten grams of crude phenylhydroxylamine, prepared by Marvel nd Kamm's method (*J. Amer. Chem. Soc.*, 1919, **41**, 276), were issolved in ether, and the sodium chloride present in the crude ɪaterial was filtered off (1 gram). The ethereal solution was first ɪturated with dry ammonia, and then, whilst the stream of mmonia was continued, a stream of methyl nitrite was led ɪrough. After a few minutes, a mass of lustrous plates began) separate, and at the end of twenty minutes the reaction was ɔmplete. The cupferron was collected, washed with a little ether, nd dried. The yield was 12 grams, which is equal to 94 per cent. f the theoretical. The material obtained gave the characteristic eactions with copper and iron.

In conclusion, the author wishes to acknowledge his thanks to ᑊrof. Lapworth for the assistance and advice which he has kindly iver during the progress of the research.

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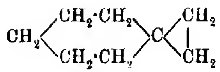
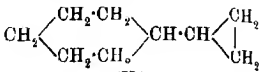
[*Received, March 26th*, 1920.]

.XIV.—*The Formation and Stability of Associated Alicyclic Systems. Part I. A System of Nomenclature, and Some Derivatives of Methane-*II-cyclo*propane and of Methane-*III-cyclo*propane.*

By RICHARD MOORE BEESLEY and JOCELYN FIELD THORPE.

ɴ a series of papers entitled "The Formation and Stability of *piro*-Compounds," of which Part II (T., 1919, **115**, 320) has ecently been published, we propose to study the reactions of those ypical substances, known as *spiro*-compounds, which have one arbon atom common to two ring systems as, for example, in the


(I.)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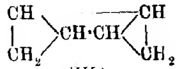
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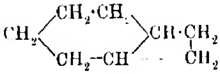
compound I. In the present series it is proposed to investigate the properties of associated ring complexes, of which compounds II, III, and IV can be regarded as typical examples. It is desirable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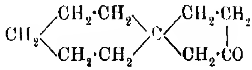

(V.)

to retain this distinction, because the *spiro*-compounds are, in their properties and reactions, quite different from ordinary ring compounds, and because they do not lend themselves to classification in accordance with the system of nomenclature which we are about to propose. Moreover, the present system for naming *spiro*-compounds is quite satisfactory, as is shown by the name 5-*cyclo*hexane-*spirocyclo*pentan-3-one, which adequately represents a compound of formula V.*

It is in the case of associated ring compounds that a really comprehensive system of nomenclature is required, because the only proposals which have hitherto been brought forward do not seem to be entirely satisfactory. Thus Baeyer (*Ber.*, 1900, **33**, 3771) has published a system in which dicyclic systems are considered. Baeyer's method depends on the fact that all dicyclic systems contain three bridged rings which render the compounds capable of being distinguished by the prefixes (0.1.2), (1.2.3), (0.1.4), and so forth, depending on whether the bridge is formed by the linking of two tertiary carbon atoms (0) or whether it is itself formed by 1, 2, or more carbon atoms (compare T., 1901, **79**, 731). This system is without doubt entirely satisfactory so far as dicyclic compounds are

* If thought desirable, the *spiro*-compounds can be included in the new system proposed. For example, compound (V) would be 3-ketobutane-$^{1:4}$II$^{1:1}$-*cyclo*hexane. In fact, the *spiro*-structure would always be indicated by the repetition of the same index figure on the ring side of the Roman numeral.

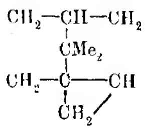
concerned, and, although Baeyer states in the last paragraph of his paper that it is also applicable to tricyclic systems, it is difficult to see how it can be extended without becoming extremely complex. Other suggestions have been made by Borsche (*Annalen*, 1910, **377**, 70) and by Bredt and Savelsberg (*J. pr. Chem.*, 1918, [ii], **97**, 1), but the systems proposed by them are open to two real objections, namely, that terms such as methylene are used to denote ring-formation and not unsaturation, and that the names of the compounds do not provide any indication of the cyclic systems to which they belong. For example, the names proposed for pinene are:

Borsche. 1-Methyl-$\Gamma^{2(4)}$-dimethylmethylene-$\Delta^{1(6)}$-*cyclo*hexene.

Bredt and *Savelsberg.* *m-meso*Methylene-4 : 4 : 2^{β}-trimethyl*cyclo*-$\Delta^{1,2\beta}$-hexene.

The name in accordance with the nomenclature proposed in this paper would be dimethylmethane-$\mathrm{II}^{1:3}$-4-methyl-Δ^4-*cyclo*hexene, indicating that the unsaturated grouping is in the *cyclo*hexane ring, and that the compound belongs to a dicyclic system (II). It is evident, moreover, that the use of the word "meso," which has another and totally different meaning, is an added objection to the system proposed by Bredt and Savelsberg.

A still more complex example may be given in the case of the hydrocarbon,

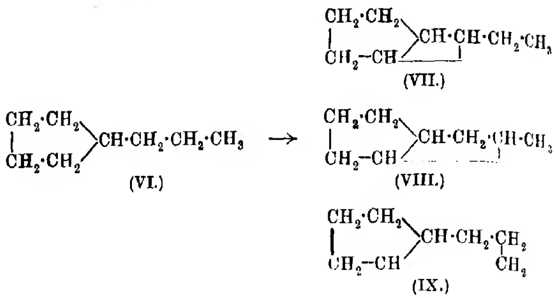


which Bredt and Savelsberg propose to call *p-meso*methylene-1 : 1-dimethyl*cyclo*hexane-*amphi*-2^a : 3^a-methylene, but would, by our system, be named methane-$\mathrm{II}^{1:2}$-*cyclo*hexane-${}^{1:4}\mathrm{II}$-dimethylmethane.

The system now proposed by us appears to be capable of indefinite extension to alicyclic compounds containing any number of associated rings. It may be briefly outlined as follows:

A compound containing associated rings may be of two kinds.

(A) It may be formed from a simple ring compound having a side-chain of carbon atoms from which another ring is produced by a linking between another carbon atom of the ring and another of the side-chain, thus:



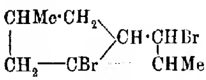
(VI.) → (VII.), (VIII.), (IX.)

In these cases the side-chain and the ring would be given their usual names, the number of linkings joining the two would be indicated by a Roman numeral and the carbon atoms of the two series participating in the ring complex would be indicated by means of index figures written at the side of the numeral on which the particular residue is placed. In this way:

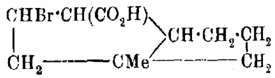
(VII) is Ethylmethane-II[1 : 2]-*cyclo*pentane.*
(VIII) is 2-Methylethane-[1 : 2]II[1 : 2]-*cyclo*pentane.
(IX) is Propane-[1 : 3]II[1 : 2]-*cyclo*pentane.

It is evident that under this scheme compound VI would be propane-[1]I[1]-*cyclo*pentane, but as this hydrocarbon does not contain associated rings there is no need to alter the existing nomenclature of the type, that is, for example, *n*-propyl*cyclo*pentane.

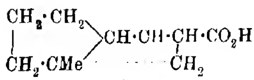
The naming of derivatives would then follow in the ordinary way, the groups in each portion being treated as at present; thus (*A*) is



(*A*.)



(*B*.)



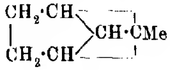
(*C*.)

1-bromo-2-methylethane-[1 : 2]II[1 : 2]-2-bromo-4-methyl*cyclo*pentane, (*B*) is propane-[1 : 3]II[1 : 2]-4-bromo-2-methyl*cyclo*pentane-5-carboxylic acid, and (*C*) is 2-carboxypropane-[1 : 3]-II[1 : 2]-2-methyl*cyclo*pentane. It will be noticed that the index figures, taken in order on either side

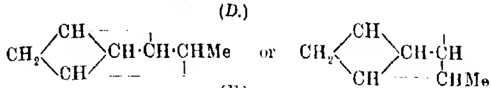
* In the case of methane derivatives it is unnecessary to show index figures on the methane side of the Roman numeral as the linkings can only emerge from one carbon atom.

of the Roman numeral, show, in each case, the actual carbon atoms linked.

If a second, third, or *n*-th ring is formed by the linking of more carbon atoms of the original ring and side-chain, the procedure is the same; thus, (*D*) is methylmethane-III$^{1:2:5}$-*cyclo*pentane, (*E*) is

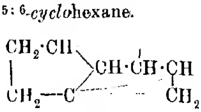


(*D*.)

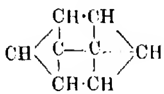


(*E*.)

2-methylethane-$^{1:1:2}$-III$^{1:2:4}$-*cyclo*butane, (*F*) is propane-$^{1:1:2:3}$IV$^{1:5:2:2}$-*cyclo*pentane, and (*G*) is ethane-$^{1:1:1:2:2:2}$VI-$^{1:2:3:4:5:6}$-*cyclo*hexane.



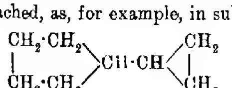
(*F*.)



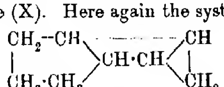
(*G*.)

It is true that this system of nomenclature could be simplified and still rendered quite intelligible by omitting the Roman numeral and leaving the index figures to denote the carbon atoms involved, thus, ethane-$^{(1:2:2)\,(1:2:5)}$-*cyclo*pentane, but it is thought that the inclusion of the numeral will make for clearness, especially when derivatives are being named; moreover, the presence of the numeral will at once indicate the class to which the compound belongs. It is also evident that the first index figure, on either side of the Roman numeral, might be omitted, because, since the numbering in each series starts with the linked carbon atoms, this must necessarily be 1 in every case. Here again, however, it is thought that the assistance given to the eye warrants its inclusion.

(**B**) The associated ring compound may be formed by linking pairs of carbon atoms in a ring to which another ring is already attached, as, for example, in substance (X). Here again the system

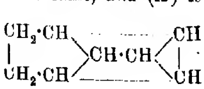


(X.)

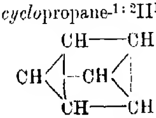


(*H*.)

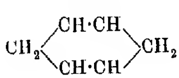
is the same, and (*H*) is *cyclo*propane-$^{1:2}$II$^{1:2}$-*cyclo*pentane, (*J*) is



(*J*.)



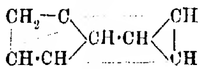
(*K*.)



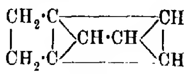
(XI.)

*cyclo*propane-$^{1:2:3}$III$^{1:2:5}$-*cyclo*pentane, (*K*) is *cyclo*propane-$^{1:2:3}$III$^{1:2:3}$-*cyclo*propane, and (XI) is *cyclo*propane-$^{1:3}$II$^{1:2}$-*cyclo*propane, the nomenclature of derivatives being the same as already illustrated under class (**A**).

It may happen that a compound can be assigned to both class (**A**) and class (**B**), but no difficulties present themselves in such cases, for example, (XII) is methane-II$^{3:4}$-*cyclo*butane-$^{1:2:4}$III$^{1:2:3}$-



(XII.)

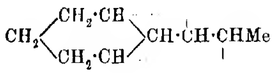


(XIII.)

*cyclo*propane, and (XIII) is ethane-$^{1:2}$II$^{2:3}$-*cyclo*propane-$^{1:2:3}$III-$^{1:2:3}$-*cyclo*propane.

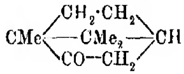
It will be noticed that compound X (p. 595) would be called, under the system proposed, *cyclo*propane-^{1}I^{1}-*cyclo*pentane, and not, as at present, *cyclo*propyl*cyclo*pentane. As in this case two associated rings are present, it is probably desirable to adopt the new method of nomenclature.

Regarding the rules to be observed when naming a compound, little ambiguity can exist in connexion with those substances which fall within class (**A**). These compounds form dicyclic systems when two linkings couple the side-chain and the ring, and tricyclic, tetracyclic systems, and so forth, when three, four, or more carbon atoms are linked together. The only rules which appear to be necessary are: (1) That one of the linked carbon atoms in the ring should be called 1, and that the corresponding carbon atom in the chain should be also called 1. The numbering would then proceed in the ring clockwise, and in the side-chain in the usual manner. (2) That the name of the simplest portion of the chain entering into ring formation should be used first, and any attached groups should be named as derivatives of the simplest chain; thus, (*L*) would be

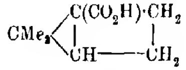


(*L*.)

2-methylethane-$^{1:2}$III$^{1:2:6}$-*cyclo*hexane, and not propane-$^{1:2}$III-$^{1:2:6}$-*cyclo*hexane, or, to take two typical examples, (*M*) would be



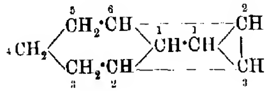
(*M*.)



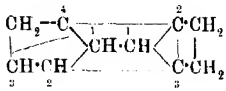
(*N*.)

dimethylmethane-II$^{1:4}$-1-methyl*cyclo*hexan-2-one, not ethane-$^{1:2}$II-

$^{1:3}$-2:2:3-trimethyl*cyclo*pentan-4-one, and (*N*) would be dimethylmethane-II$^{1:2}$-*cyclo*butane-2-carboxylic acid, and not ethane-$^{1:2}$II$^{1:3}$-2:2-dimethyl*cyclo*propane-3-carboxylic acid. With those compounds falling within class (**B**), the rules are the same. Thus the simplest ring should always be taken first, and the numbering should start from two linked carbon atoms, one in each ring, and proceed clockwise, thus, (*O*) should be *cyclo*propane-$^{1:2:3}$III$^{1:2:6}$-



(*O*.)

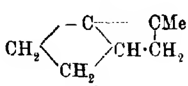


(*P*.)

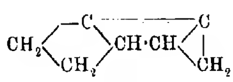
*cyclo*hexane, and not *cyclo*hexane-$^{1:2:6}$III$^{1:2:3}$-*cyclo*propane. When naming a new compound, the first point to ascertain is whether it falls within class (**A**) or class (**B**), or whether it is made up of both these types. If the latter, the system should be analysed, and the name should start with the simplest system belonging to class (**A**) involved, as in examples (XII) and (XIII) on page 596. In some highly complex cases it will again be necessary to bring in class (**A**) at the end of the name, as, for example, in the compound (*P*), in which both ends belong to class (**A**) and the middle portion to class (**B**); the name of this substance would be methane-II$^{3:4}$-*cyclo*butane-$^{1:2:4}$III$^{1:3:2}$-*cyclo*propane-$^{2:3}$II$^{1:2}$-ethane.

In some cases it will happen that a substance, whilst capable of being assigned to a single class, that is, to either (**A**) or (**B**), can also be derived from the mixed type composed of both (**A**) and (**B**). Such is the case with the compound (XI) on page 595, which can equally well be named methane-II$^{3:4}$-*cyclo*butane-$^{1:2}$II-methane. The rule should always be, however, to assign a substance to a single class, if possible, rather than to introduce the mixed type.

A system such as that outlined above seems to serve as a ready means for naming substances having associated rings, many of which are certain to be made and studied in the near future. It should be pointed out, in passing, that where double linkings occur between two carbon atoms in the system, the fact will be evident by the occurrence of consecutive recurring figures in the same positions on either side of the Roman numeral; thus, (*Q*) is 2-methylethane-



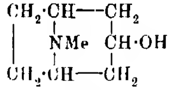
(*Q*.)

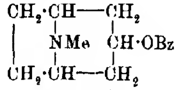


(*R*.)

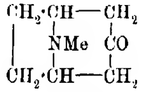
$^{1:2:2}$III$^{1:4:4}$-*cyclo*butane, and (*R*) is *cyclo*propane-$^{1:3:3}$III$^{1:2:2}$-*cyclo*propane.

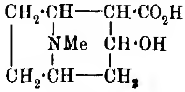
It may be added that the scheme proposed in this paper can also be applied to complex heterocyclic systems; thus, tropine would be


Tropine.

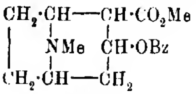

Tropacocaine.

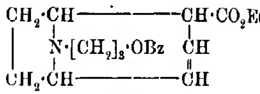
methylamine-II$^{1:5}$-3-hydroxy*cyclo*heptane, tropacocaine would be


Tropinone.


Ecgonine.

methylamine-II$^{1:5}$-3-benzoyl*cyclo*heptane, tropinone would be

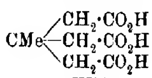

Cocaine.

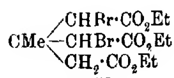

Eccaine.

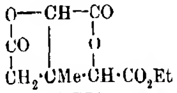
methylamine-II$^{1:5}$-*cyclo*heptan-3-one, ecgonine would be methylamine-II$^{1:5}$-*cyclo*heptan-3-ol-2-carboxylic acid, cocaine would be methyl methylamine-II$^{1:5}$-3-benzoyl*cyclo*heptane-4-carboxylate, and eccaine, ethyl γ-benzoylpropylamine-II$^{1:5}$-Δ^3-*cyclo*heptene-2-carboxylate.

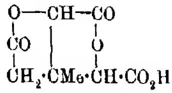
We have been led to propose this system of nomenclature in order to name certain compounds, belonging to two of the simpler series of associated rings, which are described in this paper, and for which no adequate system of nomenclature exists. A brief mention of one of these compounds was made in the *Proceedings* (1913, **29**, 346), but the war and the necessity for preparing considerable quantities of material has delayed publication until now.

The starting point is ββ-dimethylpropanetricarboxylic acid (XIV) (Thorpe and Wood, T., 1913, **103**, 1583), which can be converted into the dibromo-ethyl ester (XV) on treatment with bromine and phosphorus pentabromide under special conditions described in the experimental part. If this bromo-ester is treated with pyridine it is converted into the di-lactone ester (XVI), from which the acid (XVII) can be obtained on hydrolysis.

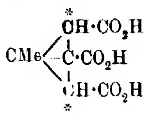

(XIV.)

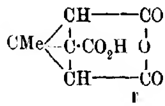

(XV.)


(XVI.)

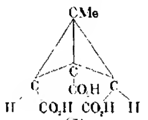

(XVII.)

If, however, the bromo-ester (XV) is treated with concentrated aqueous potassium hydroxide at a high temperature it is converted into the acid (XVIII), for which the name carboxymethane-$II^{1:3}$-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid is proposed. This acid

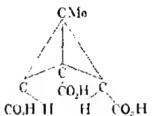

(XVIII.)


(XIX.)

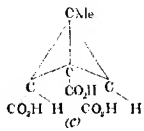
is a remarkable substance, and is, we believe, the first of its type to be prepared. It contains two asymmetric carbon atoms, marked above with asterisks, and should, therefore, exist in *cis*- and *trans*-forms corresponding with the two inactive forms of tartaric acid. On the other hand, there is no possibility of free rotation about these two carbon atoms owing to their participation in the double-ring formation. The acid should, therefore, also exist in two forms corresponding with fumaric and maleic acids. An examination of the following figures shows, however, that three inactive forms only are theoretically possible:*



(*a*)



(*b*)



(*c*)

One of these, that represented by Fig. *a*, might be expected to give an anhydro-acid with great readiness,† and, of the other two, that represented by Fig. *c* might also be expected to give an anhydro-acid, but with less readiness than the acid of Fig. *a*. The acid of Fig. *c* is, as a matter of fact, similar in structure to *cis*-norpinic acid which, as Perkin and Simonsen have shown (T., 1909, **95**, 1176), is converted into the anhydride when heated in a sealed tube with acetic anhydride at 220°. On the other hand, the acid

* The fourth possible form in the mirror image of Fig. c.

† The two asymmetric carbon atoms are evidently brought into close proximity by the closing of the second *cyclo*propane ring. This fact, which can be easily demonstrated on the models, is well illustrated by the experiments described in this paper (see note by C. K. Ingold, p. 603).

represented by Fig. *b* should not give an anhydro-acid unless the carboxyl group attached to one of the asymmetric carbon atoms entered into combination with the carboxyl group attached to the tertiary carbon atom at the far angle of the system, a contingency which, as will be shown later, is extremely unlikely because the tribasic acid (XXVIII) (p. 602), in which the third ring is formed, shows no tendency to pass into an anhydro-acid. We have therefore assigned the formula XIX to both the anhydro-acids which we have prepared.

The acid of formula XVIII can, as a matter of fact, be isolated in three distinct modifications, melting at 193°, 165°, and at 154° respectively. The acid melting at 154° passes into the anhydro-acid melting at 103° when it is heated a few degrees above its melting point. It therefore, in all probability, has a structure represented by Fig. *a*. The acid melting at 165° also gives an anhydro-acid (melting at 121°), but only does so when it is heated in a sealed tube with acetic anhydride at 200°. The acid has therefore the structure shown in Fig. *c*. Finally, the acid melting at 193°, which shows no tendency whatever to yield an anhydro-acid, in all probability has the structure given in Fig. *b*.

The anhydro-acids are each converted into the acids, from which they are derived, on boiling with water, but we have not as yet succeeded in finding the conditions under which the three acids are converted the one into the other. This is probably in part due to the fact that one cannot subject the acids to the usual conditions which convert *cis*- into *trans*-forms, such as prolonged heating with hydrochloric acid or hydrobromic acid in a sealed tube, because under these conditions all three modifications are transformed into the di-lactonic acid (XVII), a fact which clearly shows that the structures assigned to them by us are correct. There may, however, be some fundamental reason why the interconversion of these three forms is impossible, because it will be noticed that, in an acid of formula XVIII, the ring must be broken before free rotation, a condition which is presumably necessary for interconversion, can ensue, and since it is evident that the lactone form is more stable than the ring complex, it follows that all attempts to bring about interconversion of the three forms will lead to the fission of the carbon ring systems.

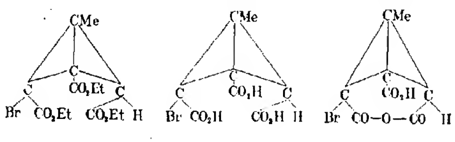
As it happens, the three acids are all produced in the original reaction and in, so far as we can judge, about equal proportions. Their separation is a simple matter because the acids themselves are insoluble in dry ether, whereas the anhydro-acids are readily soluble in this solvent. It is only necessary, therefore, to heat the mixed acids, extract the anhydro-acid of the acid melting at 154°,

then to treat the residue with acetic anhydride, and, after extracting the anhydro-acid of the acid melting at 165°, to leave the acid melting at 193° in a comparatively pure condition.*

It follows from the fact described above that an acid of formula XVIII, although containing only two asymmetric carbon atoms, can exist in three inactive forms. The mirror images of two of these forms, namely, those represented by Figs. *a* and *b*, that is to say, the acids melting at 193° and 154° respectively, are superimposable. They are therefore not resolvable. On the other hand, the mirror images of the acid represented by Fig. *c* are not superimposable, and this acid, which is that melting at 165°, is probably capable of resolution in its optical enantiomorphs. As regards their general behaviour, the three acids are comparatively stable substances. They do not, for example, reduce alkaline permanganate in the cold and do not decolorise bromine.

Except when heated in a sealed tube with either concentrated hydrochloric or hydrobromic acids, when they are converted, as already mentioned, into the di-lactonic acid (XVII), they remain unaltered even after prolonged boiling with aqueous acids or alkalis.

A very remarkable confirmation of the correctness of the formulæ assigned to these acids by us is afforded by a study of their behaviour on bromination. When, for example, the acid melting at 154° is treated with the right quantity of phosphorus pentabromide and bromine to form the monobromo-acid bromide and the product is poured into alcohol, the bromo-ester (XXI) is obtained.



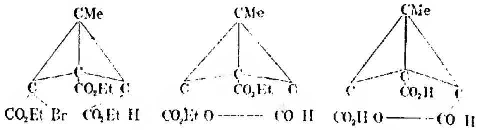
(XXI.) (XXII.) (XXIII.)

This bromo-ester is not altered by boiling pyridine, and when hydrolysed by alkali hydroxide yields the bromo-acid (XXII). The bromine atom in this compound is extremely unreactive, and is not attacked by any of the usual reagents, although the acid is readily converted into the anhydro-acid (XXIII) on treatment with acetyl chloride.

The acid melting at 165°, when treated in the same way, is con-

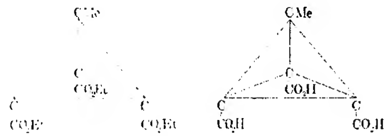
* We propose to name the acid melting at 154° the *meso-cis*-acid, that melting at 193° the *meso-trans*-acid, and that melting at 165° the racemic acid.

verted into a similar bromo-ester (XXIV), which, when boiled with pyridine, passes into the lactonic ethyl ester (XXV), from which the lactonic acid (XXVI) can be prepared on hydrolysis.



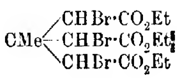
(XXIV.) (XXV.) (XXVI.)

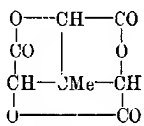
When the acid melting at 193° is treated with phosphorus pentabromide and bromine, and the product is poured into alcohol, an oil is obtained which is free from bromine. This oil is evidently the compound XXVII, since it yields the acid (XXVIII) on hydrolysis.



(XXVII.) (XXVIII.)

The acid (XXVIII), for which we propose the name methylmethane-III$^{1:2:3}$-*cyclo*propane-1:2:3-tricarboxylic acid, is identical with that already briefly mentioned in the *Proceedings* (*loc. cit.*). It is also formed, but only in small quantities, when $\beta\beta$-dimethylpropanetricarboxylic acid (XIV) is converted into its tribromo-ethyl ester (XXIX), and this is treated with concentrated aqueous alkali hydroxide at a high temperature. When boiled with pyridine, the tribromo-ester is converted into the tri-lactone (XXX) (m. p. 182°).





(XXIX.) (XXX.)

Methylmethane-III$^{1:2:3}$ *cyclo*propane-1:2:3-tricarboxylic acid could be isolated in only one form. It does not yield an anhydro-acid even when heated with acetic anhydride at a high temperature. It does not reduce alkaline permanganate in the cold, but is oxidised on heating, yielding methylsuccinic acid, together with other products which were not identified; it does not decolorise bromine. It

is stable towards boiling acids and alkalis, but when heated in a sealed tube, with either concentrated hydrochloric or hydrobromic acids, it is completely converted into the tri-lactone melting at 206° (XXX).

[The following note has been written by Mr. C. K. INGOLD.]

In the paper already mentioned (*loc. cit.*), certain alicyclic ring structures were examined in the light of the hypothesis that the resultant lines of action of the forces of valency in such carbon rings are not straight lines, but are more or less deeply curved, the amount of curvature being determined by an equilibrium in the distribution of the strains of the ring. In any ring, such as the *cyclo*propane ring represented in Fig. 1, if the whole of the

FIG. 1.

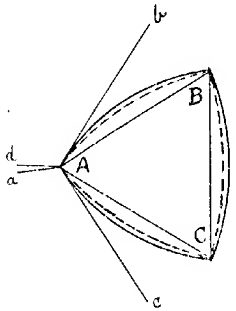
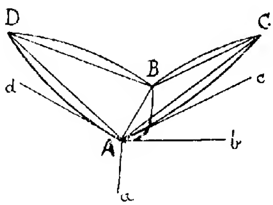


FIG. 2.



distortion were borne by the atoms, the valency resultants would lie along the shortest possible paths, the straight lines AB, BC, CA. The pair of valencies AB, AC, for example, would in this case emerge from the carbon atom A at a considerably smaller inclination than do the corresponding unstrained directions Ab, Ac. If, on the other hand, the whole of the distortion resided on the valencies, so that the directions of emergence from each carbon atom were the unstrained directions Ab, Ac, etc., inclined to one another at the normal tetrahedral angle $(2\cos^{-1}\frac{1}{3}\sqrt{3}=109^\circ 28' 16'')$, the valency resultants themselves would pursue paths of maximum curvature the terminal tangents of which are the unstrained directions in question. Previous experiments have indicated (T., 1919, **115**, 323) that the distortion lies neither wholly on the atoms nor wholly on the valencies, but partly on both, in which case the true paths of the valency resultants must be curves, such as the

dotted lines in Fig. 1 are drawn to represent, lying between the limiting straight paths on the one hand and the paths of maximum possible curvature on the other. The terminal tangents of these true (dotted) paths will therefore be inclined at each carbon atom at some angle intermediate between 60° and $2\cos^{-1}\frac{1}{3}\sqrt{3}$.

In any simple carbon ring such as the above, it is clear, both from symmetry and from the mechanical equilibrium of the carbon atoms, that all the limiting curved paths must lie in the same plane with the straight paths. The consideration of a more complex system, such as the *dicyclo*butane ring (Fig. 2), is, on the other hand, complicated by the fact that the limiting straight paths AB, BC, CA, BD, DA lie in two planes, and the limiting curved paths in three. The curved paths AC, BC, for example, will, from the mechanical equilibrium of the carbon atom, C, lie in the plane ABC. For similar reasons, the curved paths AD, BD will lie in the plane ABD. Both symmetry and the mechanical equilibrium of the carbon atoms A and B require that the curved path AB shall occupy a plane which bisects the angle between the planes of the two component *cyclo*propane rings ABC and ABD.

It is of considerable interest to calculate the angle at which the planes of the two *cyclo*propane rings are inclined. To do this, we have to consider in turn the two limiting conditions imposed by the equilibrium in the strain distribution.

Take, first, the case in which all the valency paths are straight. The carbon atom A will have its four valencies emanating in the directions Aa, AB, AC, AD. In accordance with a hypothesis which was made the subject of a previous communication (T., 1915, **107**, 1080), these four directions will set themselves in such a way that, whilst the angle BAC is 60° and the angle BAD is 60°, the angles between every other pair of valencies (namely, the angles aAB, aAC, aAD, and CAD) will be equal. Describe a sphere round A as centre, and let the lines Aa, AB, AC, AD cut it at a', B', C', D', respectively. Joining these points by arcs of great circles, we obtain the series of spherical triangles represented in Fig. 3, in which the sides $B'C'$ and $B'D'$ are each 60°, whilst the sides $a'A'$, $a'C'$, $a'D'$, $C'D'$ are all equal, say, to 2θ. The angle at B' of the spherical triangle $C'B'D'$ is the angle between the planes ABC and ABD, that is to say, it is the angle, 2ϕ, which it is intended to calculate.

From the spherical triangle $a'B'C'$ we have

$$\cos(180^\circ - \phi) = \frac{(1 - \cos 60^\circ) \cdot \cos 2\theta}{\sin 60^\circ \cdot \sin 2\theta},$$

and from the spherical triangle $C'B'D'$,

$$\cos 2\phi = \frac{\cos 2\theta - \cos^2 60^\circ}{\sin^2 60^\circ}.$$

These equations transform into

$$\frac{\sin\theta}{\sin\phi} = \sin 60^\circ$$

and

$$\frac{\cot 2\theta}{\cos\phi} = \frac{\sin 60^\circ}{\cos 60^\circ - 1}.$$

Eliminating from the last two equations the angle ϕ, we obtain a cubic in $\cos 2\theta$,

$$2\cos^3 2\theta + 2\cos^2 2\theta - 2\cos 2\theta - 1 = 0,$$

FIG. 3.

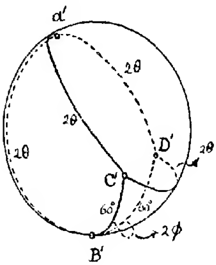
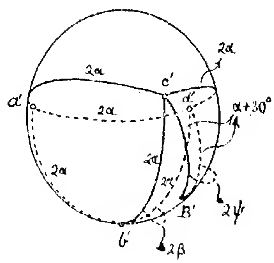


FIG. 4.



the exact solution of which is

$$\cos 2\theta = \frac{1}{3}\left[\left\{\frac{5}{4} + i\sqrt{64 - \frac{25}{16}}\right\}^{\frac{1}{3}} + \left\{\frac{5}{4} - i\sqrt{64 - \frac{25}{16}}\right\}^{\frac{1}{3}} - 1\right],$$

where i is the square root of minus one. This is the irreducible case of Cardan's solution. Extracting the real roots by De Moivre's theorem, we obtain

$$\cos 2\theta = \frac{4}{3}\cos\frac{\xi}{3} - \frac{1}{3},\ \cos 2\theta = \frac{4}{3}\cos\frac{\xi + 2\pi}{3} - \frac{1}{3},\ \cos 2\theta = \frac{4}{3}\cos\frac{\xi + 4\pi}{3} - \frac{1}{3}$$

where

$$\tan\xi = \frac{4}{5}\sqrt{64 - \frac{25}{16}}.$$

The second of these three roots leads to an imaginary value of θ. The first and third correspond with real angles, but the latter alone satisfies the pair of original equations from which the cubic was derived. We therefore have, since $\xi = 81^\circ 0' 39''$, that

$2\theta = 113^\circ 46' 4''$, and by substitution, $2\phi = 150^\circ 32' 28''$. The latter angle is the angle between the planes of the two *cyclo*propane rings calculated on the assumption that all the valency resultants follow their limiting straight paths.

Now suppose that all the valency resultants follow their limiting curved paths. The four valencies of the carbon atom A (Fig. 2) will emerge from that atom in the tangential directions Aa, Ab, Ac, Ad, inclined to one another at the normal tetrahedral angle. If we describe a sphere round A as centre and join the points a', b', c', d', in which the lines Aa, Ab, Ac, Ad cut the spherical surface by arcs of great circles, we obtain, as before, a network of spherical triangles (Fig. 4) the sides of which are all equal to $2a = 2\cos^{-1}\frac{1}{3}\sqrt{3}$. If 2β is the angle at b' of the spherical triangle $c'b'd'$, we have, as before,

$$\frac{\sin a}{\sin \beta} = \sin 2a,$$

which, since $\sin a = \dfrac{\sqrt{2}}{\sqrt{3}}$ and $\sin 2a = \dfrac{2}{3}\sqrt{2}$, gives $2\beta = 120^\circ$.

This is the angle between the planes bAc and bAd (Fig. 2). To obtain from it the angle between the planes BAC and BAD, we notice that the plane bAB bisects the angle between the planes bAc and bAd, so that if AB cuts the sphere in B' (Fig. 4), then this point must lie on the median from b' of the spherical triangle $b'c'd'$; also, if B' be joined to c' and d' by arcs of great circles, the angular distances $B'c'$ and $B'd'$ will each be $a + 30^\circ$, which completely defines the position of the point B'. The angle at B' of the spherical triangle $c'B'd'$ is clearly the angle between the planes BAc, BAd, that is to say, it is the required angle between the planes BAC and BAD. If we call the angle in question 2ψ, then from the spherical triangle $c'B'b'$ we have

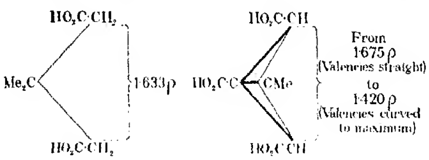
$$\frac{\sin 2a}{\sin(180^\circ - \psi)} = \frac{\sin(a + 30^\circ)}{\sin \beta},$$

in which $a = 2\cos^{-1}\frac{1}{3}\sqrt{3}$ and $\beta = 60^\circ$. Hence $2\psi = 110^\circ 9' 40''$.

The planes of the *cyclo*propane rings ABC and ABD (Fig. 2) will therefore be inclined at the angle $150^\circ 32' 28''$ or the angle $110^\circ 9' 40''$, according as the paths of the valency resultants are quite straight or curved to the maximum, and it is clear that in the latter case the carbon atoms C and D will be nearer together than in the former. In all actual cases, the inclinations of the planes and the distance between the carbon atoms C and D will lie between these limits, the precise values being determined by the strain equilibria.

The actual distance between the carbon atoms C and D can readily be calculated if we assume that a constant distance separates every pair of carbon atoms in direct combination. Mention has already been made (T., 1919, **115**, 329) of certain experiments which indicate that in condensed alicyclic rings of this kind the distance between two carbon atoms directly combined is constant, or approximately so. Assuming, then, that the distance is constant and equal to ρ, we have that the distance between the carbon atoms C and D is equal to ρ multiplied by the sine of 60° and by twice the sine of half the angle between the planes of the two *cyclo*propane rings.

It is of interest to compare this distance with the distance between the α and α' carbon atoms of a simple open-chain structure, such as *n*-propane. To take specific cases, we find that the distance between the α- and α'-carbon atoms of $\beta\beta$-dimethylglutaric acid (I) is equal to $2/3 \, . \sqrt{6} \, . \rho = 1{\cdot}633\rho$. Directly comparable with this is the distance between the tertiary carbon atoms of methyl*dicyclo*butanetricarboxylic acid (II). This works out to

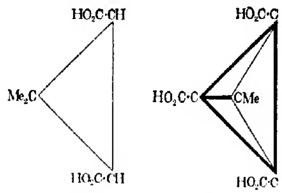


(I.) (II.) (*trans*-form.)

1·675ρ on the assumption that the ring-bound valency resultants follow their limiting straight paths, and to 1·420ρ if we assume that the resultants follow their limiting paths having maximum curvature. If, therefore, the paths of the valency resultants in the *dicyclo*butane acid (II) are straight, or practically so, then the distance between the tertiary carbon atoms should be greater than the distance between the α- and α'-carbon atoms of the glutaric acid (I). It should therefore be distinctly a more difficult matter to establish a bond between the pair of carbon atoms in question in the former compound than in the latter. On the other hand, if the valency paths in the *dicyclo*butane acid have the maximum of curvature, the distance between the carbon atoms will be much less than in the case of the glutaric acid, and it should be very much easier to bridge the *dicyclo*butane acid with the formation of the "caged" acid (IV) than it is to bridge the glutaric acid system to form the *cyclo*propane acid (III).

As a matter of fact, all the experiments described in this paper with the *dicyclo*butane acid (II) point in one direction, namely,

that the tertiary carbon atoms are much closer together than is the case with the α- and α'-carbon atoms of $\beta\beta$-dimethylglutaric acid. Bridging to form the caged acid (IV) appears to take place



(III.) (IV.)

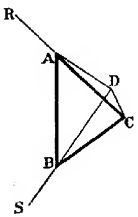
with remarkable readiness, and groups attached to the tertiary carbon atoms, if they are in *cis*-positions, possess a strong tendency to react with each other.

It is clear from what has been said that, in order to explain this result, one has to assume that the paths of the valency resultants in the *dicyclo*butane system have a considerable amount of curvature. We can place a lower limit on what this curvature must be by considering how much curvature would be necessary to give a distance between the tertiary carbon atoms of the *dicyclo*butane acid (II) equal to $1{\cdot}633\rho$, the distance between the α- and α'-carbon atoms of dimethylglutaric acid. Precise mathematical treatment would be lengthy, but an approximate estimate may be obtained if we take the curvatures of the valency paths, reckoned in per cents. of the possible maxima, to be a linear function of the distance between the tertiary carbon atoms. Calculating in this way, one finds that if the valencies of the *dicyclo*butane acid had curvatures equal to 16·5 per cent. of the maximum possible, the tertiary carbon atoms would be just as far apart as the α- and α'-carbon atoms of dimethylglutaric acid. In view of the experimental evidence, we may therefore say that the curvatures are considerably greater than 16·5 per cent. of the theoretical maxima.

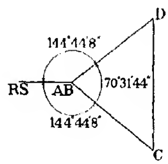
The general inference seems to be that, in agreement with the conclusions reached as a result of certain studies made with *spiro*-compounds (T., 1919, **115**, 322), the paths of the valency resultants in alicyclic rings are distinctly, and often considerably, curved. The present example is one of special interest on account of the fact that we are enabled to place a lower limit on the amount of curvature which actually exists in the constitution of the molecular structure discussed.

Whilst the above considerations lead to an intelligible view of

the experimental results, and have the merit of correlating them with certain previously ascertained facts regarding condensed alicyclic systems, there is another very simple way of looking at the present experimental data which ought not to be lost sight of in the absence of certain knowledge. One of the salient results of the experimental investigation is the great ease with which the *trans-dicyclo*butane acid passes into the "caged" acid. This fact can be strikingly brought out by making a single assumption with regard to the positions of the planes occupied by the valency directions of the carbon atoms at the ends of the bridge-bond of the *dicyclo*butane structure.



(*X.*)

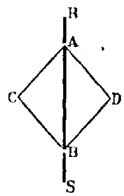


(*Y.*)

Considering, first, the caged structure $ABCD$ (formula X), let AR and BS be the directions of the free valencies attached to the carbon atoms A and B. For the sake of simplicity, we may suppose all valency directions to be straight. Taking a plan-view (formula Y) of the structure (that is, the view from some distant point on the projection of AB), we obtain three trace-lines, $(AB)(RS)$, $(AB)C$, and $(AB)D$, corresponding with the three planes $ABRS$, ABC, and ABD. If we assume that a constant distance separates every carbon atom in the "caged" structure from every other, we can show in a few steps that the angle between the planes ABC and ABD, that is, the angle $C(AB)D$ in formula Y, is $\cos^{-1}(\frac{1}{3})$, that is, $70°31'44''$. This means that the angle between each of the other pairs of planes, namely, the angles $(RS)(AB)C$ and $(RS)(AB)D$ are each equal to $144°44'8''$.

Now suppose that the bond CD is broken, and suppose that the three planes $ABRS$, ABC, and ABD maintain the same relative positions. This assumption is clearly the negation of the principle that valencies emerging from a carbon atom will set themselves so that their directions (their initial directions if they are curved) are as evenly distributed in space as possible, for it has already been noticed that the result of applying this principle to the carbon atoms A and B leads to much higher values for the

angle between the planes ABC and ABD. One might attempt to justify the assumption, however, by supposing that all carbon atoms, even when not in direct combination, attract one another, and if they are near enough originally (that is, through the structure of the substance) to be within the sphere of one another's influence, this attraction would tend to draw them nearer, and might in the present case be sufficient to prevent the planes ABC and ABD springing apart to a larger inclination when the bond CD is broken. Whether this is so or not, if the hypothesis that the planes $ABRS$, ABC, and ABD retain the same relative inclinations is tentatively accepted, we have the obvious result that the distance between the carbon atoms C and D is the same in the *dicyclo*butane structure (formula Z) as it is in the "caged" com-



(Z.)

pound. If this is really the case, it gives particularly clear significance to the remarkable degree of facility with which the "caged" substance was formed.

EXPERIMENTAL.

(1) *The Dibromination of ββ-Dimethylpropanetricarboxylic Acid. Ethyl ββ-Dibromodimethylpropanetricarboxylate* (XV, p. 599).

This bromination can be effected by adding 317 grams of phosphorus pentabromide to 50 grams of the acid contained in a Geissler flask, and then adding 80 grams of bromine gradually down the condenser tube. No bromine should be added until the contents of the flask, after the addition of the phosphorus pentabromide, have become completely liquid, and it should then be dropped into the flask very slowly, the temperature being kept as far as possible in the neighbourhood of 20°. The operation takes some little time, but it is essential to adhere to these conditions, otherwise a product containing the correct amount of bromine will not be obtained. After all the bromine has been added, the mixture may be warmed on the water-bath for half an hour, when it will be found that all free halogen has disappeared. The pro-

duct is then poured slowly into three times its volume of absolute alcohol, the temperature of the solution being kept below 25° throughout the operation. Afterwards, when the alcoholic solution has remained at the ordinary temperature for twelve hours, water is added, the precipitated oil extracted with ether, the ethereal extract thoroughly washed, first with water and then with dilute sodium carbonate solution, and the oily product isolated in the usual way.

The dibromo-ester cannot be distilled without decomposition. When, for example, it is fractionated under diminished pressure, it yields a fraction of constant boiling point passing over at 225°/15 mm., but this contains too little bromine, and can be proved to contain considerable quantities of the di-lactone ester melting at 140° (q.v.), formed by the elimination of ethyl bromide during the process of distillation. As a matter of fact, the separation of the di-lactone ester and the unchanged dibromo-ester in this mixture can be easily effected by the aid of cold benzene, in which the former is insoluble. The crude dibromo-ester is therefore not distilled prior to analysis, but purified as far as possible by placing it in an exhausted desiccator over potassium hydroxide for several days:

0·3429 gave 0·2853 AgBr. Br = 35·41.

$C_{14}H_{22}O_6Br_2$ requires Br = 35·9 per cent.

The Di-lactone of ββ-Dihydroxydimethylpropanecarbethoxydicarboxylic Acid (XVI, p. 599).

This substance can be prepared, as mentioned above, by distilling the dibromo-ester under diminished pressure, but is best obtained in quantity by boiling 60 grams of the ester mixed with 100 grams of pyridine for six hours on the sand-bath. The product is isolated by pouring it into dilute hydrochloric acid, extracting the oil with ether, and washing the ethereal extract with dilute hydrochloric acid. The residue which is left after evaporating the ether from the dried solution is an oil, which distils at 230°/20 mm. and solidifies in the receiver.

It crystallises from benzene in small, flattened needles, and from hot water in glistening plates melting at 140°:

0·1705 gave 0·3322 CO_2 and 0·0812 H_2O. C = 53·11; H = 5·29.

$C_{10}H_{12}O_6$ requires C = 52·6; H = 5·3 per cent.

The compound dissolves in cold aqueous alkalis.

The Di-lactone of ββ-Dihydroxydimethylpropanetricarboxylic Acid (XVII, p. 599).

The di-lactonic ester is readily hydrolysed when it is boiled with dilute hydrochloric acid (16 per cent. aqueous solution) for four hours, and the corresponding acid separates from the solution when it is evaporated to a small bulk. It crystallises from ethyl acetate in glistening needles, which melt at 186°:

0·1269 gave 0·2230 CO_2 and 0·0470 H_2O. C=47·92; H=4·10.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The compound is not readily soluble in cold water, but quickly dissolves on warming; it does not, however, separate from its hot concentrated aqueous solutions on cooling, and it is evident that some transformation into the hydroxy-acid takes place under these conditions. The well-defined needles fall to a fine powder, without loss of weight, when they are heated for a long time at 100°, and it is probable, therefore, that at this temperature some change in crystalline form occurs.

The *silver* salt, obtained from the neutral ammonium salt, is a white, micro-crystalline precipitate, which is evidently the salt of the dihydroxy-tribasic acid:

0·2783 gave 0·1615 Ag. Ag=58·03.
$C_8H_9O_8Ag_3$ requires Ag=58·2 per cent.

The Three Stereoisomeric Forms of Carboxymethane-$II^{1:3}$*-3-methylcyclopropane-1:2-dicarboxylic Acid* (XVIII, p. 599).

It has already been shown (T., 1915, **107**, 1096) that the action of concentrated aqueous alkali hydroxide at a high temperature leads to the formation of carbon to carbon rings, even in those compounds in which the γ-position of the bromine atoms would, under normal conditions, cause them to pass into the corresponding lactones. The formation of the above acids instead of the lactone already described furnishes another example of the efficacy of this process. Actually, under the conditions described below, no trace of the di-lactonic acid could be found in the product. Sixty grams of potassium hydroxide are dissolved in 50 c.c. of water, and the solution is evaporated over the free flame until it reaches a temperature of 150°. Fifteen grams of the dibromo-ester mixed with an equal volume of alcohol are now added as quickly as possible, consistent with safety, and the very vigorous reaction is allowed to subside. It is well to use a large flask for this operation, as the reaction is almost explosive in its violence,

and some of the material is apt to be lost by spurting. The three acids separate together when the concentrated aqueous solution is acidified with hydrochloric acid, and can be isolated in the following manner. The well-dried mixture is ground with an equal volume of clean, white sand and heated at 160°, with frequent stirring, for six hours. The cooled product is then ground, transferred to a Soxhlet apparatus, and extracted with carefully dried and purified ether. The ethereal extract, on evaporation, leaves a solid residue, which yields the meso-cis-*acid* (formula [*a*], p. 599), in slender needles, when it is boiled with a little water and the solution, mixed with an equal volume of concentrated hydrochloric acid, is allowed to cool. This acid melts at 154° and evolves steam at a few degrees above this temperature:

0·1394 gave 0·2451 CO_2 and 0·0518 H_2O. C=47·96; H=4·13.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The acid is insoluble in dry ether or benzene. It can be recrystallised from concentrated aqueous solutions, but is best purified by recrystallisation from hydrochloric acid.

The *silver* salt, prepared in the usual manner, is a white, apparently amorphous, precipitate:

0·3142 gave 0·1952 Ag. Ag=62·12.
$C_8H_5O_6Ag_3$ requires Ag=62·2 per cent.

The Anhydro-acid (XIX, p. 599, configuration [*a*]).—The acid reacts readily with acetyl chloride at the temperature of the boiling reagent, and the above substance remains as a white, crystalline solid when the chloride is evaporated. It crystallises from benzene containing a little light petroleum (b. p. 60—80°) in small plates, which melt at 103°:

0·1771 gave 0·3418 CO_2 and 0·0543 H_2O. C=52·64; H=3·41.
$C_8H_6O_5$ requires C=52·7; H=3·3 per cent.

The anhydro-acid when boiled with water yields the acid from which it was derived.

The *racemic acid* (formula [*c*], p. 599) can be isolated in a similar manner from the sand remaining in the Soxhlet apparatus, and for this purpose the sand is transferred to a glass Carius tube, mixed with a sufficient quantity of acetic anhydride, and the sealed tube heated at 220° for six hours. The product is then freed from acetic anhydride by evaporation, the residue ground, and again extracted with dry ether in a Soxhlet apparatus. In this case, it is best to purify the product left after evaporating the ether by recrystallisation from benzene, from which solvent it is obtained in lustrous plates melting at 121°. The following analysis

shows it is be the *anhydro-acid* of the racemic acid (XIX, p. 599, configuration [*c*], p. 599):

0·1737 gave 0·3344 CO_2 and 0·0531 H_2O. C=52·50; H=3·40.
$C_8H_6O_5$ requires C=52·7; H=3·3 per cent.

The anhydro-acid readily passes into solution when warmed with water, and the addition of an equal volume of concentrated hydrochloric acid precipitates the *racemic acid* in small prisms, which melt at 165°, the fused acid remaining unaltered at 300°:

0·1305 gave 0·2294 CO_2 and 0·0484 H_2O. C=47·95; H=4·12.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The acid is insoluble in dry ether or benzene. It is characterised by giving an insoluble calcium salt, which is precipitated when a neutral solution of the ammonium salt is boiled with calcium chloride solution.

The *silver* salt is similar in appearance to that of the *meso-cis*-acid:

0·2987 gave 0·1856 Ag. Ag=62·13.
$C_8H_5O_6Ag_3$ requires Ag=62·2 per cent.

The meso-trans-*acid* (formula [*b*], p. 599) can be obtained from the sandy residue on extraction with hot water, and separates when concentrated hydrochloric acid is added to the solution previously concentrated by evaporation. It is appreciably less readily soluble in water than either the *meso-cis*- or the racemic acid, and can be recrystallised from this solvent. It is, however, advisable to use dilute hydrochloric acid for this purpose, when the acid is obtained as a crystalline powder which melts at 193°:

0·1407 gave 0·2468 CO_2 and 0·0521 H_2O. C=47·73; H=4·11.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The acid does not react with acetic anhydride at a high temperature, and does not appear to possess any tendency towards anhydride formation. It can, as a matter of fact, be distilled in small quantities without undergoing any change. It is insoluble in dry ether and in benzene.

The *silver* salt is a white, sandy powder:

0·2489 gave 0·1544 Ag. Ag=62·03.
$C_8H_5O_6Ag_3$ requires Ag=62·2 per cent.

The acid forms a characteristic *calcium* salt similar in appearance to that of the racemic acid, but differing from it in being precipitated when the solution containing the neutral ammonium salt and calcium chloride is boiled, and redissolving when it is cooled.

Attempts to Convert the Three Stereoisomeric Acids into one another, leading to Fission of the Ring Systems.

All three acids remain unaltered after prolonged boiling with aqueous hydrochloric acid, and can also be recovered unchanged after having been heated in a sealed tube, in 20 per cent. aqueous solution, for six hours at 200°. When, however, 3 grams of either acid are mixed with 30 c.c. of concentrated hydrochloric or hydrobromic acid and the solution is heated in a sealed tube at 220° for ten hours, no trace of unchanged acid can be found in the product. In its place there is formed an insoluble, crystalline substance, which, after recrystallisation from ethyl acetate, is obtained in glistening needles melting at 186°. This compound is without doubt the di-lactonic acid of formula XVII (p. 599), a fact which can be shown by direct comparison and also by the following analyses:

Found: C=47·85; H=4·07.

$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

Found: Ag=58·12.

$C_8H_9O_8Ag_3$ requires Ag=58·2 per cent.

Bromination of the Three Stereoisomeric Acids.

The meso-cis-*Acid*, m. p. 154° (formula [*a*], p. 599).—The bromination of this acid proceeds very smoothly when 10 grams of the acid are treated with 64 grams of phosphorus pentabromide and 8·5 grams of bromine, the operation being carried out in the usual way at the ordinary temperature, and being finished by warming on the water-bath. The product, when poured into well-cooled alcohol, yields an oil on dilution with water, which can be extracted with ether. The washed and dried extract leaves cis-*ethyl bromocarbethoxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylate* (XXI, p. 601) on evaporating the solvent. The bromo-ester distils without decomposition at 207°/12 mm., and is a clear, fairly mobile oil:

0·1813 gave 0·0930 AgBr. Br=21·83.

$C_{14}H_{19}O_6Br$ requires Br=22·0 per cent.

The bromo-ester is recovered unchanged even after prolonged boiling with pyridine, but when hydrolysed by boiling with an alcoholic solution containing one and a-half times the calculated quantity of potassium hydroxide, it is hydrolysed to cis-*bromocarboxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylic acid* (XXII, p. 601), which can be isolated by evaporating the solution

free from alcohol, acidifying, and filtering. This acid crystallises from hot water in small needles, which melt at 171°:

0·2203 gave 0·1473 AgBr. Br=28·45.

$C_8H_7O_6Br$ requires Br=28·6 per cent.

The *bromo-anhydro-acid* (XXIII, p. 601) is readily obtained from the above bromo-acid by boiling it for an hour on the water-bath with excess of acetyl chloride, and is left as a crystalline residue when the reagent is evaporated. It crystallises from benzene in colourless plates, which melt at 139°:

0·1910 gave 0·1373 AgBr. Br=30·59.

$C_8H_5O_5Br$ requires Br=30·7 per cent.

The anhydro-acid when boiled with water yields the acid from which it was derived. It should be added that in all the three compounds described above, the halogen is very strongly combined, and is, in fact, almost aromatic in character. For example, the usual test by boiling with fuming nitric acid and silver nitrate in a test-tube fails to reveal the presence of bromine in them.

The Racemic Acid, m. p. 165° (formula [*c*], p. 599).—This acid is brominated in precisely the same way as the *meso-cis*-acid, and it gives r-*ethyl bromocarbethoxymethane*-$II^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylate* (XXIV, p. 602) with equal readiness. The ester undergoes partial decomposition on distillation under diminished pressure, and it is therefore best to use the crude product, which can be sufficiently purified by placing it in an exhausted desiccator over potassium hydroxide for some days:

0·1994 gave 0·1018 AgBr. Br=21·71.

$C_{14}H_{19}O_6Br$ requires Br=22·0 per cent.

The bromo-ester reacts quickly when it is boiled with three times its volume of pyridine for three hours, and the product can be isolated by pouring the mixture into excess of dilute hydrochloric acid and extracting with ether. The dried ethereal extract leaves a solid residue on evaporation, which is the *lactone* of *hydroxycarbethoxymethane*-$II^{1:3}$-3-*methyl*cyclo*propane*-1-*carbethoxy*-2-*carboxylic acid* (XXV, p. 602), a substance which crystallises from benzene in small needles melting at 87°:

0·1365 gave 0·2832 CO_2 and 0·0689 H_2O. C=56·59; H=5·61.

$C_{12}H_{14}O_6$ requires C=56·7; H=5·5 per cent.

The lactonic ester dissolves in cold aqueous alkalis, and, if a sufficient quantity of the reagent is used, it is hydrolysed at the boiling point in the course of an hour. The solution, after being freed from alcohol by evaporation, is acidified, when the *lactone* of *hydroxycarboxymethane*-$II^{1:3}$-3-*methyl*cyclo*propane*-1 : 2-*dicarb-*

oxylic acid (XXVI, p. 602) is precipitated. The compound crystallises from benzene in groups of needles and melts at 137°:

0·1420 gave 0·2519 CO_2 and 0·0398 H_2O. C=48·38; H=3·12.
$C_8H_6O_6$ requires C=48·5; H=3·0 per cent.

The *silver* salt, prepared from a neutral solution of the ammonium salt, is evidently that of the tribasic hydroxy-acid:

0·2417 gave 0·1454 Ag. Ag=60·15.
$C_8H_5O_7Ag_3$ requires Ag=60·3 per cent.

The lactonic acid does not separate well either from water or from dilute hydrochloric acid. The corresponding hydroxy-acid could not be isolated.

The meso-trans-*Acid*, m. p. 193° (formula [*b*], p. 599).—The method of bromination is the same as that given in the case of the *meso-cis*-acid, and the operation proceeds with the same readiness. When, however, the product is poured into alcohol, it will be found that the oil which is subsequently precipitated by the addition of water is free from bromine. When collected in the usual way and fractionated under diminished pressure, it yields *ethyl methylmethane*-III$^{1:2:3}$-cyclo*propane*-1 : 2 : 3-*tricarboxylate* (XXVII, p. 602) as a colourless, fairly mobile oil boiling at 183°/12 mm.:

0·1501 gave 0·3268 CO_2 and 0·0879 H_2O. C=59·37; H=6·51.
$C_{11}H_{18}O_6$ requires C=59·6; H=6·4 per cent.

Methylmethane-III$^{1:2:3}$-cyclo*propane*-1:2:3-*tricarboxylic Acid* (XXVIII, p. 602).

The hydrolysis of the tribasic ester is effected by boiling it with an alcoholic solution containing 1·5 times the theoretical quantity of potassium hydroxide for two hours, and is obtained by acidifying the solution after it has been freed from alcohol by evaporation. The acid is purified by recrystallisation from dilute hydrochloric acid. It forms small, well-defined prisms, which melt at 149°:

0·1702 gave 0·3020 CO_2 and 0·0475 H_2O. C=48·40; H=3·10.
$C_8H_6O_6$ requires C=48·5; H=3·0 per cent.

The *silver* salt, prepared from the neutral ammonium salt, is a white, micro-crystalline precipitate:

0·2003 gave 0·1247 Ag. Ag=62·25.
$C_8H_3O_6Ag_3$ requires Ag=62·4 per cent.

The acid is freely soluble in warm water, but is insoluble in ether or benzene. It is not acted on by acetic anhydride at a

high temperature, and can be distilled in small quantities at the ordinary pressure without undergoing change. There is, apparently, no tendency whatever for it to pass into an anhydro-acid. It is stable towards bromine, even when heated, and does not decolorise alkaline permanganate in the cold, although it is slowly attacked by the boiling reagent, and, from the products, methylsuccinic acid, melting at 112°, can be isolated (Found: C=45·28; H=6·18. $C_5H_8O_4$ requires C=45·4; H=6·1 per cent.). It is not affected by prolonged boiling with aqueous acids or alkalis. An attempt was made to convert the acid into an isomeride by heating it in a sealed tube with concentrated hydrochloric acid for ten hours at 220°, and under these conditions it is converted into another substance, which separates in a crystalline condition when the contents of the tube are cooled. This compound is not, however, a stereoisomeride, but is the *tri-lactone* of *α-hydroxy-ββ-dihydroxydimethylpropanetricarboxylic acid* (XXX, p. 602), which can be recrystallised from a large quantity of benzene and obtained in ill-defined crystals melting at 206°:

0·1667 gave 0·2957 CO_2 and 0·0467 H_2O. C=48·39; H=3·11.
$C_8H_6O_6$ requires C=48·5; H=3·0 per cent.

The *silver* salt, prepared from the neutral ammonium salt, is a white, amorphous precipitate, and is evidently the salt of the trihydroxy-tribasic acid:

0·2179 gave 0·1230 Ag. Ag=56·44.
$C_8H_9O_9Ag_3$ requires Ag=56·5 per cent.

The lactone is soluble in warm water, but does not crystallise well on cooling, although the separation is facilitated by the addition of an equal volume of concentrated hydrochloric acid to the concentrated aqueous solution. It is probable that solution in water converts some of the lactone into the hydroxy-acid, although all attempts to prepare this acid were unsuccessful.

(2) *The Tribromination of ββ-Dimethylpropanetricarboxylic Acid.*

The method is the same as that described in the case of dibromination, only 120 grams of bromine are used in place of 80 grams. The final atom of bromine is absorbed with considerable difficulty, and it is advantageous, after adding sufficient bromine to form the dibromo-compound, to add the remaining molecule at once, and to leave the mixture at 60° for twenty-four hours before final completion on the water-bath. Care must, of course, be taken to exclude moisture throughout this operation by the provision of a calcium chloride tube at the end of the con-

denser. It will be found, moreover, that the rate of absorption is increased if a trace of iodine is added.

The product is then poured into well-cooled alcohol, and the oil precipitated by water in the usual manner, the ethereal extract being washed with water and then with sodium carbonate solution. The residue left after the evaporation of the dried ethereal solution contains too little bromine (Found: Br=36·31. $C_{14}H_{21}O_6Br_3$ requires Br=45·7 per cent.), and it is, therefore, in all probability mixed with either the di- or the tri-lactone. That this is actually the case can be shown by mixing the oil with an equal volume of benzene, when a crystalline solid slowly separates. The filtrate deposits more of this solid on keeping, and this, after collection, leaves a filtrate which, when freed from the solvent, consists of *ethyl α-bromo-ββ-dibromodimethylpropanetricarboxylate* (XXIX, p. 602) in an approximately pure condition:

0·2101 gave 0·2190 AgBr. Br=44·36.

$C_{14}H_{21}O_6Br_3$ requires Br=45·7 per cent.

Unfortunately, the bromo-ester cannot be distilled without undergoing decomposition, and the above product is the purest form of the compound we were able to prepare.

The solid material obtained in the above purification yields a small quantity of the tri-lactone, melting at 206°, when repeatedly recrystallised from benzene, but it also contained other compounds, which we were not able to isolate in a pure condition.

Action of Pyridine.—When the tribromo-ester is boiled with three times its volume of pyridine and the product is poured into dilute hydrochloric acid, a crystalline substance slowly separates, which is shown to be the *tri-lactone* of *α-hydroxy-ββ-dihydroxydimethylpropanetricarboxylic acid* (XXX, p. 602), melting at 206°, by direct comparison and by the following analysis:

Found: C=48·31; H=3·06.

$C_8H_6O_6$ requires C=48·5; H=3·0 per cent.

Action of Concentrated Aqueous Potassium Hydroxide.—The operation is the same as that described in the case of the dibromo-ester (p. 610). The product, when acidified, yields a crystalline precipitate, from which, by repeated recrystallisation from dilute hydrochloric acid, a small quantity of *methylmethane*-$III^{1:2:3}$-cyclo*propane*-1:2:3-*tricarboxylic acid* (XXVIII, p. 602), melting at 149°, can be isolated (Found: C=48·38; H=3·12. $C_8H_6O_6$ requires C=48·5; H=3·0 per cent.), the yield being only 12 per cent. of that theoretically possible. The remainder of the product of this reaction is undoubtedly the tri-lactone (XXX, p. 602),

as this substance can be isolated in considerable quantities from the acid mother liquors.

Many of the experiments described in this paper were carried out at the University of Sheffield by Mr. A. S. Wood, to whom our thanks are due.

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LXV.—*Colouring Matters of Red and Blue Fluorite.*

By CECIL STEVENSON GARNETT.

IN a recent paper, Blount and Sequeira (T., 1919, **115**, 705) showed that a minute amount of organic matter could be extracted from "Blue John" by means of various solvents, and draw the conclusion that the colour of the mineral is of organic origin

The experiments now to be described appear to confirm the above conclusion, but also carry the investigation somewhat further.

A quantity of extremely deep blue fluorite was discovered by the author near the famous "Blue John Mine" some years ago; the colour was uniform, and so deep that at a short distance a small lump appeared almost as black as coal. On very thin slices being cut from this material, however, it was seen to be of a beautiful deep blue, its apparent blackness being due to extreme depth of colour. Spar of this character is not sent from the mine from which the previous authors obtained their specimens.

A sample was finely powdered and extracted successively with chloroform, benzene, and ether, and although there was no apparent diminution in colour, it would be difficult to say that this was not the case, as in fine powder even so dark a specimen had such a pale blue colour that a slight further diminution in tint would scarcely be perceptible. The carbon content determined by combustion was 0·27 per cent. before, and 0·207 per cent. after, extraction. Similar determinations on other samples showed a decrease in carbon content with a decrease in colour. The amount of carbon found in the very dark specimen is nearly five times the

amount contained in the specimen quoted by Blount and Sequeira (0·046 per cent.).

The powdered mineral, when heated with concentrated sulphuric acid, yielded a black, carbonaceous residue, but when heated with a mixture of sulphuric and nitric acids, the blue compound was readily oxidised, leaving a colourless residue of fluorite (and, of course, calcium sulphate). When heated alone, a very pronounced bituminous odour was observed, and a residue of clear, colourless fluorite remained; the odour was quite different from the resinous one produced by heating specimens of "Blue John" which have been polished and made into fancy goods.

Distillation of "Blue John."

The actual separation of bituminous matter was next attempted. A hard-glass tube was almost filled with the powdered, extracted fluorite, and a small U-tube (merely air-cooled) attached. On heating, a yellowish-brown oil collected in the cool parts of the apparatus, and an inflammable gas issued from the jet. The gas burned steadily and freely until the distillation had proceeded to completion, when a residue of colourless fluorite remained. The inside of the glass tube had, however, gained a mirror-like coating of carbon, evidently resulting from the decomposition of the vapour after being driven from the fluorite and on coming in contact with the red-hot walls of the tube.

The removal of the colouring matter without the deposition of carbon within the tube was now attempted, and was easily accomplished by immersing the tube containing the powdered fluorite in a bath of molten tin. Oil again collected, but much less inflammable gas was obtained, and no deposition of carbon occurred on the walls of the tube. The removal of the colouring matter was, in these experiments, evidently accomplished only by its destructive distillation.

In order to ascertain the distribution of the colouring matter within the fluorite, thin sections were examined microscopically. It was observed that the colouring matter is not homogeneously distributed in a fine state of division within the fluorite crystals, but that it occurs as films therein. The depth of colour depends on the abundance and thickness of the films existing in the fluorite, which is itself clear and colourless. They occur parallel to and in the plane of the faces of the crystal (cube), and also at the crystalline junctions, in such a manner as to point to the conclusion that the colouring matter was deposited as films on the surfaces of the crystals at intervals during their growth. The banded coloration

of "Blue John" is explained by this supposition. The blue colour imparted by the bituminous matter is probably due to the chemical combination in which the latter exists.

Red Fluorite.

Mawe ("Mineralogy of Derbyshire," 1802) states that ruby-coloured fluorite in perfect cubes is said to have been found in Derbyshire. No other occurrence of this rare variety of fluorite in Derbyshire appears to have been observed until the present author recorded having found a quantity of it near Ashover. The colour of this specimen is not pink, as are the specimens usually seen in museums, but definitely red.

The colour of this variety is not due to organic matter, and the appearance is scarcely altered by prolonged exposure to a bright red heat. The colouring matter is readily and completely extracted from the roughly crushed fluorite by boiling hydrochloric or nitric acids, leaving a residue of clear, colourless fluorite. The solution was found to contain rare earths and nothing but insignificant traces of any other element. The oxalates and sulphates were obtained as usual, and an attempt was made to separate and identify the rare earth elements present, but was not continued, on account of the well-known difficulties which such a task presents.

Microscopical examination of thin sections showed that the colouring matter is distributed as films in colourless fluorite. Instead, however, of the films occurring chiefly within the crystal (as in the case of "Blue John"), they appear to exist chiefly (at least) at the crystalline junctions within the mass (as in the case of fluorite coloured brown by limonite). The redness of the colour is due to the thinness of the films, as the mineral of which they consist may be occasionally found in tiny cavities in the fluorite; it is massive, black, opaque, and pitch-like in appearance. Microscopical examination of films of varying thickness (as they occur) confirms the chemical evidence as to the identity of the black, "rare earth" mineral and the films.

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LXVI.—*Studies in Catalysis. Part XIII. Contact Potentials and Dielectric Capacities of Metals, in Relation to the Occlusion of Hydrogen, and Hydrogenation.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

IN two earlier papers in this series (T., 1919, **115**, 182, 1360), heterogeneous catalysis was considered from the point of view of the critical increment and the radiation hypothesis of chemical reactivity. It was pointed out that the essential function of such a catalyst was to reduce greatly the critical increment of activation of one or more of the reactants, thereby increasing the rate of the reaction. The effect was considered as induced at the surface of the catalyst on which at least one of the reactants was adsorbed. The same idea is obviously applicable to any case in which one or more of the reactants is capable of being actually dissolved by the catalyst and emitted from its surface in the activated form. Such a case is encountered in the activation of hydrogen as a result of occlusion by certain metals.

The Critical Increment, E_{H_2} of Dissociation of Hydrogen into Atoms when dissolved in a Metal.

In an extended series of papers, Sieverts has measured the solubility of hydrogen in various metals over a wide range of temperature. He has found that, in general, the concentration of the dissolved gas varies as the square root of the pressure of hydrogen in the gas phase, indicating that the hydrogen is dissociated into atoms or ions. The most trustworthy results are those obtained with nickel, iron, and copper (*Zeitsch. physikal. Chem.*, 1911, **77**, 591), in which it was found that the solubility of hydrogen is higher in nickel than in iron, and greater in iron than in copper. Sieverts has shown that the process is one of true solubility, and not simply surface adsorption, although the latter is necessarily present as well.

The solubility of hydrogen in these and in other metals increases markedly as the temperature rises. Applying the well-known thermodynamic relation to the variation of the solubility, S, with the temperature, we have

$$d \log S / dT = Q / RT^2,$$

where Q stands for the heat absorbed in the process at constant volume. Postulating that the process is

$$H_2 \longrightarrow 2H,$$

and assuming, as has been done in another connexion, that the critical increment of union of the free atoms is zero, it follows that Q is identical with E_{H_2}, the critical increment of dissociation per gram-molecule of hydrogen in the dissolved state. From Sieverts' values of the solubility of hydrogen, it is thus possible to calculate E_{H_2} at various temperatures. The following results have thus been obtained. The solubility, S, is expressed in milligrams of gas per 100 grams of metal.

Nickel.

t.	S.	$d \log S/dT$.	E_{H_2} in cals.
315°	0·22	$3·05 \times 10^{-3}$	2099
822	0·72	$1·66 \times 10^{-3}$	3984
1225	1·333	$1·30 \times 10^{-3}$	5824

In the neighbourhood of 150°, E_{H_2} is calculated to be approximately 1700 cals. It will be observed that as the temperature rises the value of E_{H_2} also increases. This is discussed later.

Iron.

t.	S.	$d \log S/dT$.	E_{H_2}.
514°	0·075	$5·3 \times 10^{-3}$	6560
775	0·201	$3·0 \times 10^{-3}$	6590

In the neighbourhood of 150°, E_{H_2} is estimated to be 6500 cals.

Copper.

t.	S.	$d \log S/dT$.	E_{H_2}.
620°	0·030	$5·0 \times 10^{-3}$	7975
827	0·072	$4·2 \times 10^{-3}$	9080
904	0·102	$4·0 \times 10^{-3}$	11080
981	0·132	$3·8 \times 10^{-3}$	11930

In the neighbourhood of 150°, E_{H_2} is of the order of 5000 cals. It is impossible to extrapolate with accuracy, as the experimental results at the lowest temperatures are evidently somewhat discordant.

Platinum (Sieverts, *Ber.*, 1912, **45**, 221).

t.	S.	$d \log S/dT$.	E_{H_2}.
1136°	0·036	$4·4 \times 10^{-3}$	17480
1239	0·055	$4·2 \times 10^{-3}$	19200

Actual extrapolation to low temperatures is impossible in this case. It is evident, however, that E_{H_2} in the neighbourhood of 150° lies between 10,000 and 15,000 cals.

In general, the lower the solubility the greater is the critical increment. A large critical increment means that the metal in question has a relatively small dissociating power.

It must be emphasised that the values in the last table refer to absorption by metallic platinum. If hydrogenation is due to atomic hydrogen which has been brought into existence by the act of dissolving, it follows that metallic platinum is a less efficient catalyst than copper. In the case of platinum-black, however, Mond, Ramsay, and Shields (*Phil. Trans.*, 1896, [*A*], **186**, 657) have shown that the quantity of hydrogen absorbed is very much greater than it is in massive platinum, and, further, that the quantity absorbed diminishes as the temperature rises. In the case of platinum-black, we are probably dealing with adsorption alone.

Sieverts has shown that hydrogen is soluble in cobalt, the solubility becoming measurable above 700°. The same author has also found that hydrogen is insoluble in pure silver. Similarly, in the case of gold, the solubility is too low to be measured. Hydrogen is likewise insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, and aluminium (compare *Zeitsch. Elektrochem.*, 1910, **16**, 708). Aluminium, however, forms a hydride above 800°. One would expect those metals in which hydrogen is insoluble to be negative catalysts for hydrogenation if they partly or wholly cover the surface of the catalytically active metal.

On the view advanced in the present paper, the conclusion is that the insolubility of hydrogen in the metals mentioned is due to the inability of these metals to dissociate the gas.

The solubility of hydrogen in tungsten is extremely low (Sieverts, *Ber.*, 1911, **44**, 2394). On the other hand, the solubility of hydrogen in tantalum is very high, and diminishes as the temperature rises, although proportional to the square root of the hydrogen pressure. The case is analogous to that exhibited by palladium over a certain temperature range, a compound being formed which dissociates with absorption of heat.

The Variation of E_{H_2} with Temperature, and the Dielectric Capacity of the Metal.

As the foregoing calculations show, the apparent critical increment of dissociation of molecular hydrogen rises steadily as the temperature increases. The simplest explanation of this is to

assume that the dissociating power of the metal diminishes as the temperature rises, this being the usual effect of temperature on this property. From the point of view of electrostatic attractions between the constituent parts of a dissolved molecule, we should expect, in accordance with the Thomson-Nernst rule, that the value of E_{H_2} would vary inversely as the dielectric capacity of the metal or inversely as the square of the refractive index of the wave-length corresponding with the value of E. To dissociate molecular hydrogen in the gaseous state into atoms requires an absorption of 85,000 cals. per gram-molecule. If atomic hydrogen is formed in metals, it would follow that the dielectric capacity, D_0, of nickel, for example, in the region of 150° is given by the relation

$$1700 = 85000/D_0,$$

whence $$D_{Ni} = 50.$$

Similarly, $$D_{Fe} = 13,\ D_{Cu} = 17,$$

and $$D_{Pt} = 6 \text{ to } 8.$$

On the classical electromagnetic theory, the dielectric capacities of metals were regarded as infinite. This conclusion has been shown not to be necessary by Sanford (*Physical Rev.*, 1918, [ii], **12**, 130), who concludes from experiments on contact electrification that metals possess dielectric capacities of the same order of magnitude as those of non-metals. In Sanford's experiments, no precautions appear to have been taken to remove surface films (adsorbed moisture and gases), so that the estimated magnitude of D is probably incorrect.

If it could be shown that a true Volta potential difference exists between two pure metals in contact, this would point to the reality of finite dielectric capacities. The problem of the existence of such potential differences has been under discussion since the time of Volta himself. Within recent years, however, the evidence obtained from the study of thermionic currents and photo-electric effects has lent very strong support to the original view of Volta. This evidence is discussed in detail by Langmuir (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 129), who has shown that several independent methods lead to substantially the same values for the contact potential. Langmuir's conclusions regarding the real existence of such potential differences appears to be incontrovertible.

Calculation of the Contact Potential Difference on the Basis of a Finite Dielectric Capacity attributed to a Metal.

As shown by Langmuir, the contact potential difference which comes into existence when two metals are brought into intimate

contact can be regarded as the difference of two "imaginary" potential differences, each of which is characteristic of a given metal. This potential difference, which may be called conveniently the *characteristic potential* of a metal, and is denoted by the symbol Φ is a measure of the forces which hold an electron in the metal and prevent its escape. It is "imaginary" in the sense that it does not come into existence until the electron is in the act of leaving the surface. The values of Φ for a number of metals have been obtained from observations on thermionics, the threshold frequency of the normal photo-electric effect, and line-spectra resonance measurements, the results being concordant.

If we assume the existence of a finite dielectric capacity as characterising a metal, it should be possible to calculate the work done in removing an electron from the metal to free space, thereby obtaining a value of Φ which may be compared with the mean value given by Langmuir. Let us denote by W the work required to extract an electron and bring it into free space, theoretically at infinite distance from the metal surface. Employing the inverse square law, which is known to hold down to distances of the order of atomic dimensions, although not down to nuclear and electronic dimensions, we obtain

$$W = e^2 \int_{r_0}^{\infty} \frac{dr}{Dr^2}$$

where D is the dielectric capacity at any position r. The dielectric capacity alters continuously as we pass from the metal to free space, its value being D_0 in the metal and unity in free space. The simplest mode of allowing for this variation is to write

$$D = D_0^{r_0/r}$$

where r_0 is the average distance apart of an electron and a metallic ion in the metal. Lindemann (*Phil. Mag.*, 1915, [vi], **29**, 127) has put forward a number of considerations for regarding the metallic state as being composed of two interwoven space lattices, one an electron lattice, the other an ionic one. On the average, an electron will be separated from an ion by a distance r_0, which is one half the distance between two contiguous ions. Langmuir (*loc. cit.*) has pointed out that in the case of the simple face-centred cubic lattice, which is characteristic of copper and silver, the shortest distance, σ, between two adjacent atoms is given by

$$\sigma = 1{\cdot}33 \times 10^{-8} . V^{1/3}$$

where V is the atomic volume. From the values of σ thus calculated by Langmuir, we can obtain the value of r_0.

On integrating the expression for W, we obtain

$$W = \frac{e^2}{r_0 \log_e D_0}\left(1 - \frac{1}{D_0}\right).$$

This must be equivalent to Φe, whence

$$\Phi = \frac{e}{r_0 \log_e D_0}\left(1 - \frac{1}{D_0}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We have now to evaluate this expression for certain metals, using the approximate values of D_0 which we have obtained for the temperature 150°.

Copper.—$D_0 = 17$. $\sigma = 2{\cdot}56 \times 10^{-8}$ cm. Hence $r_0 = 1{\cdot}28 \times 10^{-8}$. 1 E.S.U. $= 3 \times 10^2$ volts. Hence $\Phi = 3{\cdot}8$ volts.

The weighted mean value obtained by Langmuir from the results of various observers is $\Phi = 4{\cdot}0$ volts.

Iron.—$D_0 = 13$. $= 2{\cdot}56 \times 10^{-8}$ cm. Hence $r_0 = 1{\cdot}28 \times 10^{-8}$. Hence $\Phi = 3{\cdot}5$ volts.

Langmuir's value is 3·7 volts.

Platinum.—$D_0 = 7$ approximately, whence $\Phi = 4{\cdot}97$ volts. Langmuir gives the value 4·4 volts with a query. Values greater than 5 volts have been obtained by various observers.

In general, the agreement between the accepted value of Φ and that calculated by means of equation (1) is satisfactory. To this extent we are justified, therefore, in attributing a finite dielectric capacity to a metal.

Nickel.—$D_0 = 50$. Taking r_0 to be the same as that for copper, we find that $\Phi = 2{\cdot}8$ volts. The characteristic potential for nickel has not as yet been determined by any direct method. It follows from the above value that if copper and nickel are brought into contact, the nickel should be positive with respect to the copper, the contact potential difference being $3{\cdot}8 - 2{\cdot}8 = 1$ volt.

From the observed values of Φ quoted by Langmuir, we can calculate the dielectric capacity of the corresponding metal by means of equation (1). We thus find the following values in a few typical cases:

Metal.	Φ in volts.	$r_0 \times 10^8$.	D_0.
Silver	4·1	1·45	8
Zinc	3·4	1·40	18
Aluminium	3·0	1·45	30
Lithium	2·35	1·57	40
Sodium	1·82	1·91	60

It is evident from the above values that the dielectric capacity does not completely determine the solubility of hydrogen in a metal. Thus, metals such as zinc, bismuth, and tin possess higher dielectric capacities than platinum, yet hydrogen is soluble in

platinum and insoluble in these metals. It is noteworthy that the alkali metals, which apparently possess very high dielectric capacities, are capable of forming hydrides. Aluminium, which also has a fairly high capacity, forms a hydride at higher temperatures. This cannot be a general rule, however, for nickel does not apparently form a hydride. We must seek, therefore, some other factor as an equally significant quantity.

The capability of a metal of dissolving hydrogen, and, in the limit of forming a hydride, depends, not only on the dielectric capacity, but also on the type of radiant energy which the metal is able to supply to dissociate the gas when the latter has entered the surface. In virtue of the temperature of the metal, all types (frequencies) of radiation are present, although to very different extents. The metal is capable of enhancing the density of certain types, thereby increasing the dissociating effect provided the frequencies are sufficiently high.

Source of the Energy which Dissociates Hydrogen in a Metal.

The atoms of a metal possess energy in respect of vibration and also in respect of rotation (Honda, *Sci. Rep. Tohoku Imp. Univ.*, 1918, 7, No. 2), the latter being a negligible quantity so far as specific heats are concerned, until high temperatures are reached. Honda considers that the act of fusion, and the latent heat connected therewith, depend on this energy of rotation. If an atom possessing the amount of energy corresponding with its latent heat of fusion is brought to rest, this energy will be emitted. The author suggests that this is the source of the energy which brings about dissociation of the hydrogen in the metal. In this connexion, it is noteworthy that the metals which are capable of dissociating hydrogen are those with the highest values for the latent heat of fusion. The following table contains some of the values quoted by Honda:

Metal.	Latent heat of fusion per gram-atom L.	D_0.	$D_0 \times L$
Pt	5360	Ca 7	37,520
Pd	3860	—	—
Fe	3348	13	43,524
Ni	2710	50	135,500
Cu	2650	17	45,050
Ag	2270	8	18,160
Al	2160	30	64,800
Zn	1840	18	33,120
Cd	1540	—	—
Pb	1118	—	—
Na	730	60	43,800
Hg	562	—	—

If all metals possessed the same dielectric capacity, the value of the latent heat of fusion should distinguish those metals which dissolve hydrogen from those which do not. The dielectric capacity varies, however, from metal to metal, with the result that even sodium is capable of forming a hydride, and therefore of dissolving or dissociating the gas. The dissociating power depends simultaneously on the dielectric capacity and the density of the suitable energy. If the dielectric capacity is small, the energy required is correspondingly great, and the available energy of the type considered may be insufficient, especially as the higher the latent heat of fusion the fewer are the number of atoms at a given temperature which possess the corresponding energy. Thus, tungsten appears to have the highest characteristic potential of any element so far investigated. This means that tungsten has a very low dielectric capacity, and, consequently, the energy required to dissociate and dissolve the hydrogen is high. Although the latent heat of fusion of tungsten is greater than that of platinum (as inferred from the value of $\nu_{max.}$ of the Debye equation), it is evidently incapable of dissociating the hydrogen to any measurable extent, for Sieverts has found the solubility of the gas to be exceedingly low. The determining factor in regard to the behaviour of the metal towards hydrogen would seem to be given by the product of the dielectric capacity and the latent heat. In respect of this product, the metals arrange themselves in the following order, commencing with the highest value of the product:

Ni, Al, Cu, Na, Fe, Pt, Zn, Ag.

It is evident that those metals which can dissociate or react with hydrogen possess the higher values for the product. In the case of nickel, we have no independent value of Φ, and therefore no value of D_0 independent of the solubility method made use of to calculate D. Its position in the series is therefore not significant.

When we compare the energy, represented by L, with the value of E_{H_2}, we see that, especially at higher temperatures, more than one atom of the metal, in general two atoms, are required to contribute the energy necessary for dissociation of hydrogen. In the case of sodium at low temperatures, if we take the value for D_0, namely, 60, which is obtained from the resonance potential, we conclude that the energy required to dissociate one gram-molecule of hydrogen in sodium is $85{,}000/60 = 1420$ cals. Calculated for one gram-atom of hydrogen, the energy required is 710 cals., which is just capable of being furnished by the L term of sodium.

On the basis of the suggestion that the energy represented by the latent heat of fusion is the origin of the dissociation of hydrogen in metals, it would follow that the solubility of the gas

in the molten metal should be considerably greater than in the solid. This is in agreement with the experimental results of Sieverts (*Zeitsch. physikal. Chem.*, 1911, **77**, 591), who has found that at the melting point of the metal, the solubility of hydrogen in molten copper is three times as great as it is in the solid, and twice as great in molten nickel and iron as it is in the solid. Further, the increase of solubility with temperature is greater for the molten than for the solid metal.

Variation of the Characteristic Potential of Metals with Temperature.

On the basis of the formula deduced for Φ, (equation [1]), it may be concluded that, in general, the greater the value of the dielectric capacity, the smaller the value of the characteristic potential. Since the dielectric capacity diminishes as the temperature rises, the value of Φ should increase slowly as the temperature rises. The effect of the variation of D_0 is, however, partly compensated by the change in r_0. Owing to the temperature-coefficient, it is not strictly correct to compare the calculated values of Φ with those obtained from the photo-electric effect at the ordinary temperature. The possible error in D_0 (which is obtained from the solubility of hydrogen in the metal) is such, however, as to render this objection less cogent. The temperature-coefficient of the dielectric capacity of metals is distinctly less than that for non-metals.

Hydrogenation.

It is evident that the property possessed by certain metals of dissolving hydrogen in the atomic form is closely related to the known catalytic power of the same metals for the hydrogenation of unsaturated compounds. This view, which is no longer novel, was definitely stated by Sieverts in 1910 as a result of his series of researches, some of which have been considered in the preceding part of this paper. Although stress is thus laid on the fact of solubility of hydrogen in certain metals, it is not intended to identify solubility itself with catalytic efficiency. The latter must depend ultimately on obtaining hydrogen or other gases in the active state, preferably the atomic state, at the surface of the metal. It is evident, however, that the property which enables a metal to dissolve and to dissociate hydrogen will likewise cause a similar activation of the gas at the surface, so that although large adsorbing surface is the necessary condition for the catalytic effect, the well-known specific influence of the metallic catalyst is

to be inferred from its capacity of dissolving and dissociating th gas. Nickel and cobalt, for example, in the finely divided form are known to occlude very much larger quantities of hydrogen tha the same mass of metal in compact form (compare Sieverts, *Zeitsch. physikal. Chem.*, 1907, **60**, 178), the effect being obviously an adsorption, the extent of which is dependent in turn on the specific nature of the metal, as indicated by its solvent power.

Among the numerous investigations of the mechanism of hydrogenation of unsaturated fats and oils, mention may be made of those recently carried out by Thomas (*J. Soc. Chem. Ind.*, 1920, **39**, 10T) and by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137, 322).

In connexion with the function of the catalyst (nickel), Thomas has applied the author's radiation hypothesis of chemical reactivity. The reaction is found to be unimolecular with respect to olein, and from the temperature-coefficient of the velocity-constant, corrected for the increase in solubility of the hydrogen in the metal with rise in temperature, Thomas has calculated that the critical increment amounts to 3820 cals. per gram-molecule of olein converted. This quantity is ascribed by Thomas entirely to the activation of the olein molecule. In view, however, of the numerical data obtained for the activation of hydrogen in nickel, it would appear necessary to deduct the energy required for the hydrogen. Thomas has found experimentally that the rate of the reaction varies as the 1·5 power of the hydrogen pressure in the apparatus, that is, three hydrogen atoms are required for one molecule of olein. The amount of energy required to dissociate one gram-molecule of hydrogen in nickel at 150° has been estimated in the present paper to be approximately 1700 cals. Consequently to produce three gram-atoms, 2500 cals. are required. On subtracting this from the total critical increment obtained by Thomas namely, 3820 cals., we obtain 1300 cals. as the critical incremen of the olein. This quantity, expressed in terms of wave-lengths o radiation, corresponds with 21 μ. Since the maximum of th temperature radiational energy at 150° occurs at about 7 μ, it i evident that a considerable number of the olein molecules ar activated to the required stage by the temperature of the syste itself. That is, a catalyst is unnecessary for the activation of th olein.

In thus ascribing the energy term, 1300 cals., to the activatio of the olein molecules, it is implied that diffusion has not to t taken into account. This is in agreement with the view put fo ward by Thomas, who remarks that the vigorous shaking to whic

the olein–nickel mixture was subjected in his experiments excludes diffusion as a significant factor.

Thomas has made the remarkable discovery, already mentioned, that the rate of hydrogenation of olein is proportional to the pressure of the molecular hydrogen in the apparatus raised to the 1·5 power. It follows, as Thomas points out, that three atoms of hydrogen take part in the hydrogenation of one molecule of olein. The fact that this is an odd number is significant, as it involves the primary formation of a molecule midway in composition between olein and stearin. This half-saturated molecule possesses, necessarily, either one or three free valencies, which will cause the spontaneous formation of an apparently saturated bimolecular form having the composition $[C_3H_5(C_{18}H_{34}O_2)_3]_2$. The author is unaware whether any such intermediate stage has been observed. This bimolecular compound could, of course, decompose into a molecule of stearin and a molecule of olein.

Returning to the question of the temperature-coefficient, it may be pointed out that, on the above view, its numerical value should be considerably greater if copper were used as a catalyst in place of nickel. Thus, on the basis of the earlier considerations in this paper, we conclude that the amount of energy required to dissociate one gram-molecule of hydrogen in copper is of the order of 5000 cals. To produce three gram-atoms of hydrogen would require, therefore, 7500 cals. To this has to be added the energy of activation of olein, namely, 1300 cals., making in all a critical increment of 8800 cals. In the neighbourhood of 200°, it follows that the temperature-coefficient for an interval of 10° would be 1·21 (when corrected for the variation of the solubility of hydrogen in copper), whilst its value in the case of nickel is less than 1·13. At the same time, the velocity-constant with copper as catalyst would only be of the order 5×10^{-3} of the velocity with nickel.

It may be pointed out that the efficiency of nickel in respect of dissolving and dissociating hydrogen has been related to its dielectric capacity and the latent heat of fusion. This affords a certain amount of guidance in a search for a possibly more effective catalyst, which would probably be an alloy.

As regards the mechanism of hydrogenation, the first and essential stage would appear to be the formation of atomic hydrogen, this being accomplished by actual solution in, or by adsorption of, the gas on the surface of the metal. The second stage is to bring the olein molecule to the surface of the metal at which active hydrogen already exists. That is, collision of the olein (already activated in virtue of its temperature) with the

metal particle must take place. The final stage is the addition of atomic hydrogen at the moment of collision. These stages may be represented thus:

Hydrogen + nickel $\longrightarrow$ atomic hydrogen available at the surface.
Olein molecule + nickel charged with hydrogen $\longrightarrow$
collision $\longrightarrow$ hydrogenation.

The fact that hydrogenation commences without a period of delay in such cases as olein indicates that the first stage, namely, production of atomic hydrogen, occurs rapidly. If the metal were completely covered by or united with the unsaturated compound before hydrogen was admitted, it would be impossible for hydrogenation to occur. This effect, "negative auto-catalysis," which is theoretically possible, evidently does not occur with olein and similar substances. In these circumstances, the measurable reaction which defines the rate of hydrogenation appears to be the second, namely, the rate of collision of the unsaturated compound with the catalyst. The collision frequency per c.c. per second of these two substances is given on the kinetic theory of gases by

$$\pi\sigma_1\sigma_2\sqrt{u_1^2+u_2^2}\,.\,N_{\mathrm{Ni}}\,.\,N_{\mathrm{olein}},$$

where σ_1 and σ_2 are the radii of the olein molecule and of the nickel particle, u_1 and u_2 the root-mean-square velocity of the olein molecule and the nickel particle, N_{Ni} the number of nickel particles per c.c., and N_{olein} the number of molecules of olein per c.c. Since the concentration of nickel is kept constant throughout any reaction, the above expression leads to a unimolecular velocity-constant.

The above expression, which gives the total number of collisions between nickel particles and olein molecules, does not allow for the fact that the resulting chemical change likewise depends on the critical increment term which defines the number of "favourable" collisions. The actual rate of the chemical process on the above basis would be given by

$$\pi\sigma_1\sigma_2\sqrt{u_1^2+u_2^2}\,.\,N_{\mathrm{Ni}}\,.\,N_{\mathrm{olein}}\;e^{-E/RT},$$

where E, obtained from Thomas's measurements, is 5576 cals. at 135° and 5228 cals. at 165°. These numbers are the fictitious values of E, which are obtained when no allowance is made for the change of the solubility of hydrogen in nickel with temperature. It is necessary to employ these values, and not the corrected value 3820 cals., when direct comparison with experimental velocity-constants is desired.

The number of favourable collisions, that is, the number of

molecules of olein hydrogenated when expressed as a fraction of the total number of olein molecules present, is given by

$$\pi\sigma_1\sigma_2\sqrt{u_1^2+u_2^2}\,.\,N_{Ni}\,.\,e^{-E/RT},$$

which should be identical with the observed unimolecular velocity-constant.

An attempt will now be made to apply this equation to the hydrogenation of olein by finely divided nickel at 180°. At this temperature the value of E is 5000 cals. in round numbers. The quantity with which the largest error is likely to be associated is that represented by σ_2, the average radius of the nickel particles. A quantity of finely divided nickel was examined under the microscope by Mr. L. E. Campbell in this laboratory. The sizes of the different individuals varied greatly. On preparing a suspension of the same sample of nickel in glycerol, the coarsest particles fall to the bottom, and, on withdrawing small quantities of the liquid at various levels and examining them, a more uniform appearance was obtained. It was found that the particles consisted in the main of individual units having a diameter of approximately 2×10^{-4} cm., together with a smaller number of larger aggregates of approximately ten times this size, each aggregate having a porous structure, being apparently built up of the smaller units. We are probably justified, therefore, in employing the value 5×10^{-4} as indicating the order of magnitude of σ_2; it is impossible to make a more exact estimate at the present time. Taking the density of nickel as 8·8, the mass of a single average nickel particle is $4{\cdot}4\times10^{-9}$ gram. Hence, in the case of olein containing 1 per cent. of nickel in suspension, the number of particles of nickel per c.c. $=N_{Ni}=2\times10^6$. The mass of an olein molecule is $1{\cdot}5\times10^{-21}$ gram, which is extremely small compared with the mass of a nickel particle. Consequently, we can neglect u_2, the velocity of the metallic particle compared with u_1, the velocity of an olein molecule.

The term $\sqrt{u_1^2+u_2^2}$ becomes, therefore, u_1, which at 180° is equal to $1{\cdot}1\times10^4$ cm. per second. The radius of the olein molecule is known to be 6×10^{-8} cm. The term $e^{-E/RT}=3{\cdot}85\times10^{-3}$. Hence

$$\pi\sigma_1\sigma_2u_1N_{Ni}e^{-E/RT}=8\times10^{-3}.$$

The observed velocity-constant at $180°=3{\cdot}4\times10^{-4}$, time being expressed in seconds and natural logarithms being employed. The calculated value is therefore twenty-four times the observed. If σ_2 were taken to be 10^{-3} cm. instead of 5×10^{-4} cm., the calculated velocity-constant would be 2×10^{-3}, which is six times the observed. In spite of the discrepancy, which may be well attributed to an

error in the size assumed for the nickel particle, for, according to the above expression, the velocity varies inversely as the square of the radius of the particle, the result might be regarded as prima facie evidence for the treatment of the problem on the basis of collisions. Velocity data with graded nickel of approximately uniform grain are apparently not available.

The above mechanism only requires collision between a single olein molecule and a single nickel particle, the latter being charged with atomic hydrogen. Of the total collisions, only a small fraction, namely, $\epsilon^{-E/RT}$, is effective for the chemical change. If permanent adsorption of olein as a result of collisions occurred, we should have expected a still higher velocity than that calculated, which already errs in the sense of being too high. True adsorption of the olein, therefore, apparently does not take place, the adsorption and solution phenomena being restricted to the nickel and hydrogen system. The absence of adsorption of the olein is in agreement with the results obtained by Armstrong and Hilditch on the hydrogenation of carbon monoxide to methane, although these authors regard the mechanism from a somewhat different point of view. Even when the concentration of the carbon monoxide is small, the effect takes place in the presence of olein, and, "moreover, the amount of change is as much, if not more, than the amount which takes place under similar conditions in absence of oil." Naturally, the nature of the unsaturated substance, olein, linolein, etc., determines the rate of the reaction, since the total critical increment, E, contains a term characteristic of the substance undergoing change. This is in agreement with one of the conclusions drawn by Armstrong and Hilditch. Further, since cotton-seed oil, linseed oil, whale oil, and olive oil contain more than one unsaturated substance, this introduces a change in the value of E during the course of a given reaction. In the case dealt with above, however, Thomas has determined the velocity-constants of the two constituents of olive oil, olein and linolein, and the collision equation has been applied to the single substance olein, as this forms 90 per cent. of olive oil, and presumably the data obtained for this substance are the most trustworthy.

The mechanism of hydrogenation assumed as a working hypothesis in the foregoing paragraphs involves essentially the dissociation of hydrogen, either adsorbed on or absorbed by the nickel, followed by collisions between the charged nickel particles and the unsaturated molecules. It is not intended to suggest that in all cases collision frequency is the determining factor. It appears to be so in the case of olein, and presumably of similar substances. In other cases there is the possibility of adsorption of

the unsaturated substance. In the latter cases, the observed rate of reaction would be expected to be considerably greater than that given by the collision equation, the degree of applicability of the expression being made use of as a criterion for the absence or presence of adsorption. Either view would also lead us to expect dehydrogenation of a saturated compound in the absence of hydrogen, since nickel will tend to abstract hydrogen from the compound in order to attain an equilibrium between hydrogen, unsaturated substance, and saturated substance. Under ordinary conditions of hydrogenation, in which hydrogen is used in large excess, the equilibrium point is necessarily shifted far to one side. For those cases to which the collision expression applies, the equilibrium-constant would be expected to take the form:

$$\frac{\text{equilibrium concentration of unsaturated compound} \times \text{concentration of charged Ni}}{\text{concentration of saturated compound}}$$

that is, the equilibrium *constant* would not depend on the amount of nickel present in the system. If, on the other hand, adsorption is a significant term, the above equilibrium expression is meaningless. In either case, we should expect that the best hydrogenating agent would likewise be the best dehydrogenating agent.

Summary.

(1) From a consideration of the solubility of hydrogen in certain metals, it is inferred that metals in general possess finite dielectric capacities.

(2) Values for the dielectric capacities of a number of metals at various temperatures have been obtained from the critical increments of dissociation of hydrogen dissolved therein, by making use of the fact that 85,000 cals. per gram-molecule is the critical increment of dissociation of hydrogen in the free, gaseous state.

(3) The insolubility of hydrogen in certain metals is regarded as being due to the inability of these metals to dissociate the gas. For this reason, these metals may be expected to function as negative catalysts when deposited on the surface of active metals in hydrogenation.

(4) An expression has been obtained for the characteristic potential at the surface of a pure metal, namely,

$$\Phi = \frac{e}{r_0 \log_e D_0}\left(1 - \frac{1}{D_0}\right),$$

where e is the charge on an electron, r_0 the average distance of an electron from its neighbouring ion in the metal, and D_0 is the

dielectric capacity of the metal. This expression is found to be in satisfactory agreement with the accepted values of Φ, the latter being obtained from thermionic effects, the threshold frequency of the normal photo-electric effect, and the resonance potential of metallic vapours. This agreement is regarded as supporting the view of the existence of finite dielectric capacities in the case of metals. By means of the above equation, it is calculated that Φ for nickel is 2·8 volts. The contact potential difference between two pure metals is necessarily the difference of their Φ values.

(5) In addition to the dielectric capacity, it is shown that the dissociating power of a metal for hydrogen depends on the existence in the metal of radiation of a sufficiently short wave-length. This is shown to be related to the magnitude of the atomic latent heat of fusion of the metal, a measure of the dissociating power being given by the product of the dielectric capacity and the latent heat of fusion.

(6) In the light of the foregoing conclusions, the mechanism of hydrogenation of olein by nickel and other metals is considered, the processes involved consisting primarily of the dissociation and solution or adsorption of hydrogen by the particles of the metal with which the olein molecules, which are already activated in virtue of their temperature, collide. It is found that a simple collision expression of the following form reproduces, in so far as order of magnitude is concerned, the observed unimolecular velocity-constants obtained by Thomas (*loc. cit.*):

$$k = \pi\sigma_1\sigma_2 u_1 N_{Ni} e^{-E/RT},$$

where σ_1 is the mean radius of the olein molecule, σ_2 the corresponding quantity for an average particle of nickel, u_1 the mean thermal velocity of the olein molecule, and E is the uncorrected critical increment of the reaction, that is, the critical increment observed directly by experiment, uncorrected for the variation with temperature of the solubility of hydrogen in the metal. It is concluded that, in the case of hydrogenation of olein and of similar substances, adsorption of the unsaturated compound on the metal does not take place, the adsorption being restricted to the metal–hydrogen components.

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LXVII.—*The Preparation of* cyclo*Heptane*-1 : 1-*di-acetic Acid.*

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IN two recent papers (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080; Ingold and Thorpe, T., 1919, **115**, 320), a comparison was made between derivatives of $\beta\beta$-dimethylglutaric (I) and *cyclo*-

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix} \qquad \begin{matrix}\mathrm{Me}\\ \mathrm{Me}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

(II.) (I.)

hexanediacetic acid (II) with respect to the degree of ease with which a bond can be established between the two α-carbon atoms of the acid, and the stability of the trimethylene compounds so produced.

From the experimental data, it is argued that the forcing apart of two of the valencies of the quaternary carbon atom from 109°28′ to 120°, consequent on the formation of a *cyclo*hexane ring, has the effect of diminishing the angle between the other two valencies, thus bringing the two $\cdot CH_2\cdot CO_2H$ groups attached to the quaternary carbon atom into closer proximity. This facilitates the closing of a trimethylene ring, and, moreover, the

$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix} \qquad \mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH\cdot CO_2H}\\ |\\ \mathrm{CH\cdot CO_2H}\end{matrix}$$

spiro-compound so produced is more stable than the corresponding trimethylene derivative, caronic acid (III).

$$\begin{matrix}\mathrm{Me}\\ \mathrm{Me}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH\cdot CO_2H}\\ |\\ \mathrm{CH\cdot CO_2H}\end{matrix} \qquad \begin{matrix}\mathrm{CH_2\cdot CH_2\cdot CH_2}\\ |\\ \mathrm{CH_2\cdot CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

(III.) (IV.)

It is obvious that this effect should be even more marked in the case of a compound in which two of the valencies of the quaternary carbon atom are forced still farther apart by participating in the formation of a seven- or eight-membered ring, the angle in these cases being, according to Baeyer's strain theory, 128°34′ and 135° respectively.

The interest attaching to the question has led the present authors to study the best conditions for the preparation of *cyclo*-

heptanediacetic acid (IV), which would serve as the starting point in an investigation of the problem.

From analogy to similar acids containing five- or six-membered rings, it was thought that the desired acid could be readily obtained by condensing suberone with cyanoacetamide by Thole and Thorpe's method (T., 1911, **99**, 422) and hydrolysing the product, or with ethyl cyanoacetate and ammonia in alcoholic

$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>CO + \begin{array}{l}NH_2\cdot CO\cdot CH_2\cdot CN\\ CN\cdot CH_2\cdot CO\cdot NH_2\end{array} =$$

$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C<\!\!\begin{array}{l}CH(CO\cdot NH_2)\cdot C(NH)\\ CH(CN)\text{------------}CO\end{array}\!\!>NH,$$

solution by Guareschi's method (compare Kon and Thorpe, T.,

$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>CO + \begin{array}{l}CN\cdot CH_2\cdot CO_2Et\\ CN\cdot CH_2\cdot CO_2Et\end{array} + 2NH_3 \longrightarrow$$

$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C<\!\!\begin{array}{l}CH(CN)\cdot CO\\ CH(CN)\cdot CO\end{array}\!\!>NH$$

(V.)

1919, **115**, 686), the latter product being also readily hydrolysed to the acid.

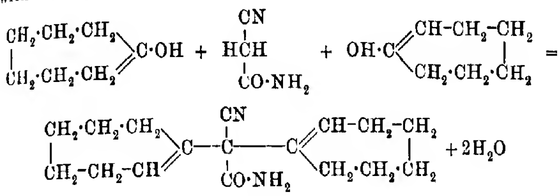
The necessary quantity of suberone was therefore prepared, but it was found that this ketone failed to react with cyanoacetamide under the conditions used by Thole and Thorpe in similar cases.

Guareschi's method was therefore adopted, but it was found that a yield of scarcely 15 per cent. of the theoretical was the best that could be obtained under the different conditions tried, and it generally amounted to about 10 per cent. only.

The reason of the unsatisfactory yields is at present without explanation. It may be due to the solubility of the ammonium salt of the dicyano-imide, which is not precipitated from the alcoholic solution, as is the case in other condensations of a similar nature; but it is also conceivable that the effect of a seven-membered ring may be to inhibit the closing of a piperidine ring in the same way and for the same reason as it may be expected to facilitate the formation of a three-membered ring, that is, by reducing the angle between the two valencies of the quaternary carbon atom which do not take part in the formation of the seven-membered ring.

An examination of the mother liquor from the original condensation has led to the discovery, in addition to cyanoacetamide and unchanged ketone, of a compound apparently formed from one molecule of the former and two molecules of the latter by the

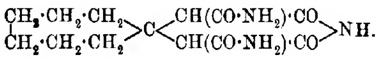
elimination of two molecules of water, doubtless in accordance with the following scheme:



(VI.)

although the experimental data are as yet insufficient to establish the constitution with certainty.

An examination of the main condensation product showed that it was formed in the usual manner from one molecule of the ketone reacting with two molecules of cyanoacetamide (see p. 640). It possessed the usual properties of such compounds, crystallised well, and gave on treatment with cold concentrated sulphuric acid the diamide,



(VII.)

On complete hydrolysis by means of boiling 85 per cent. sulphuric acid, a fair yield of *cyclo*heptanediacetic acid was obtained from the imide.

The acid, which melts at 156—157°, greatly resembles its homologues, *cyclo*hexanediacetic acid (Thole and Thorpe, *loc. cit.*, p. 445) and *cyclo*pentanediacetic acid (Kon and Thorpe, *loc. cit.*, p. 700), and was characterised by the formation of its *anhydride* and *semianilide*, which crystallise very readily.

Experimental.

Preparation of Suberic Acid.

Markownikov's method (*Ber.*, 1894, **26**, 3089) was followed. One hundred kilos. of dilute nitric acid (D 1·25) were gradually added to 50 kilos. of castor oil contained in a large steam-jacketed pan; each addition of the acid caused considerable frothing, so that the operation occupied several days; the contents of the pan were finally heated for another day.

The aqueous layer was then syphoned out, and the gummy oil repeatedly extracted with boiling water. The combined aqueous solutions were evaporated to dryness, yielding about 5 kilos. of a dark solid still contaminated with oily matter.

The whole quantity was purified by dissolving it in water, boiling with animal charcoal (500 grams of crude acid, 750 c.c. of water, and 40 grams of animal charcoal), rapidly filtering, and allowing to crystallise. The solid so obtained was sandy in appearance and melted indefinitely between 110° and 130°; the quantity was 3000 grams, which includes some recovered by extracting the charcoal with hot water.

Preliminary experiments showed that Markownikov's method of separating suberic and azelaic acids by means of ether (*loc. cit.*) was extremely tedious and unsatisfactory, and an attempt was made to find a simpler method. This was ultimately achieved, enabling sufficiently pure suberic acid to be produced in one operation.

Three hundred grams of mixed acids, purified as above, are suspended in 1500 c.c. of boiling benzene and brought into solution by adding absolute alcohol (about 390 c.c. were usually required). On cooling, almost pure suberic acid, melting at 136—138°, separates out, and can be used for the preparation of suberone without further purification.

A second crystallisation is sufficient to give pure, although still somewhat coloured, suberic acid, melting at 139—140° (Found: C=55·01; H=7·83. $C_8H_{14}O_4$ requires C=55·18; H=8·05 per cent.).

The separation of the acid was usually hastened by leaving the vessel in a cool place overnight, and it was found that the yield varied somewhat with the temperature, but was usually about 120 grams; if it was much higher, the quality of the product was inferior.

The mother liquors from the first crop of suberic acid were evaporated to half their bulk and allowed to crystallise again; from the solid which separated, more suberic acid could be obtained by repeating the process described above. The total amount of suberic acid produced in this way was 1500 grams.

The combined mother liquors on evaporation yielded a residue, from which, after removing the oily impurities by rubbing twice with dry ether and pressing on porous plates, azelaic acid could be obtained in a state of purity by repeated crystallisation from water (m. p. 106°; Found: C=57·42; H=8·30. $C_9H_{16}O_4$ requires C=57·44; H=8·51 per cent.), but the quantity was rather small (200 grams).

Preparation of Suberone.

The catalytic process of the Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 256622), which was found to give such excellent

results in the case of adipic acid (Kon and Thorpe, *loc. cit.*), could not be applied to suberic acid, the latter distilling unchanged; the modification involving the use of iron filings instead of baryta as a catalyst was also unsatisfactory. The following method was finally adopted.

The suberic acid was converted through its ammonium salt into the calcium salt, using a 20 per cent. excess of lime. The salt was carefully dried at 100° and distilled in portions of not more than 28 grams at a time.

The best vessel for the purpose was found to be a 500 c.c. conical flask suspended in an iron saucepan serving as an air-bath, and provided with an asbestos cover perforated to allow the neck of the flask to protrude.

The flask was provided with a cork with two tubes passing through. One of these enabled a current of an inert gas to be circulated through the apparatus, whilst the other, which penetrated half way down into the flask and consisted of capillary tubing (compare Young, T., 1891, **59**, 621), served as a still-head, and was connected to the condenser. This arrangement minimises the decomposition, which is caused by the distillate dropping back on to the hot calcium salt in the flask.

Four such sets of apparatus enabled 1400 grams of suberic acid to be worked up in a few days.

The crude distillate was separated from the small amount of water and fractionated, the fractions obtained from the total amount of suberic acid being as follows:

(1).........	Below 100°	8 grams
(2).........	100—160°	15 ,,
(3).........	160—174	21 ,,
(4).........	174—183	362 ,,
(5).........	183—190	31 ,,
(6).........	190—200	26 ,,
(7).........	200—240	20 ,,

Fraction (4) was pure enough to condense with ethyl cyanoacetate. An attempt was made to purify fraction (5) through the semicarbazone, but this led to loss; the bisulphite method, however, proved very satisfactory, and a further 50 grams of pure suberone were obtained from the fractions of high and low boiling points.

*Condensation of Suberone with Ethyl Cyanoacetate: ω-Imide of $\alpha\alpha_1$-Dicyano*cyclo*heptane*-1 : 1-*diacetic Acid* (V, p. 640).

As already mentioned in the introduction, only a very poor yield of the above condensation product could be obtained by the Guareschi method, and the ketone, which had failed to react, had to be recovered by a long and tedious process.

The best results were obtained as follows: 44 grams of suberone,

90 grams of ethyl cyanoacetate, and 200 c.c. of saturated alcoholic ammonia were mixed and kept in a stoppered bottle for three days. The mixture deposited a certain amount of cyanoacetamide and assumed a deep yellow colour. It was mixed with about 800 c.c. of water, and the aqueous layer twice extracted with ether and acidified, when 11 grams of a crystalline solid were precipitated, and 1·5 grams were recovered by evaporating the mother liquor to half its bulk.

On recrystallisation from dilute alcohol, the compound is obtained in colourless, sparkling plates melting at 203·5—204°:

0·1133 gave 0·2637 CO_2 and 0·0646 H_2O. C=63·71; H=6·31.
0·1045 „ 15·95 c.c. N_2 at 19·5° and 757·7 mm. N=17·38.
$C_{13}H_{15}O_2N_3$ requires C=63·64; H=6·17; N=17·14 per cent.

ω-Imide of $\alpha\alpha_1$*-Dicarbamyl*cyclo*heptane*-1 : 1-*diacetic Acid* (VII, p. 641).

If the above dicyano-imide is dissolved in ten times its weight of cold concentrated sulphuric acid, and the solution, after remaining for twenty-four hours, is poured on ice, a crystalline solid is gradually deposited. It forms transparent prisms blackening at 295° and decomposing without melting at about 305°:

0·0914 gave 11·9 c.c. N_2 at 19·5° and 765·6 mm. N=14·98.
$C_{13}H_{19}O_4N_3$ requires N=14·94 per cent.

It is very sparingly soluble in all solvents, but can be recrystallised from a large quantity of acetic acid.

cyclo*Heptane*-1 : 1-*diacetic Acid* (IV, p. 639).

Twenty grams of the dicyano-imide are dissolved in 70 c.c. of concentrated sulphuric acid, 15 c.c. of water are added, and the solution is gently heated on a sand-bath until a vigorous evolution of carbon dioxide begins; the temperature is then kept steady for about an hour until the reaction slackens, when the liquid is allowed to cool; 50 c.c. of water are then added, and the solution is boiled under reflux for five hours. When cold, the solution is diluted with water and repeatedly extracted with ether, the acid being removed from the ether by shaking with sodium carbonate solution; it is precipitated when the latter is acidified (13·5 grams).

The acid obtained in this way crystallises well from dilute alcohol in long, flattened needles, which melt at 156—157°. It is very sparingly soluble in water or benzene, differing in the latter property from the isomeric methyl*cyclo*hexanediacetic acids, which are appreciably more readily soluble in benzene:

0·1282 gave 0·2902 CO_2 and 0·0980 H_2O. C=61·73; H=8·49.
$C_{11}H_{18}O_4$ requires C=61·64; H=8·46 per cent.

A neutral solution of the ammonium salt of the acid gives no recipitate with a normal solution of barium chloride. With alcium chloride, a precipitate is obtained on boiling the solution, nd this does not redissolve on cooling or adding water.

The *silver* salt is obtained as a curdy precipitate on adding a olution of silver nitrate to a neutral solution of the ammonium alt. It is very sparingly soluble:

0·3025 gave 0·1515 Ag. Ag = 50·08.

$C_{11}H_{17}O_4Ag$ requires Ag = 50·42 per cent.

The *anhydride* is readily formed by the action of boiling acetyl chloride on the acid, and crystallises in large laminæ as the reagent evaporates. It separates from light petroleum (b. p. 60—80°) in iridescent plates melting at 75—76°, and is slowly reconverted to the acid on boiling with water:

0·1189 gave 0·2940 CO_2 and 0·0883 H_2O. C = 67·41; H = 8·25.

$C_{11}H_{16}O_3$ requires C = 67·35; H = 8·22 per cent.

The *semianilide* is prepared by boiling a benzene solution of the anhydride with aniline for a few minutes. It crystallises on evaporating off the benzene, and can be purified by recrystallisation from dilute alcohol. It forms small plates melting at 139·5—140°:

0·1321 gave 0·3409 CO_2 and 0·0957 H_2O. C = 70·37; H = 8·05.

$C_{17}H_{23}O_3N$ requires C = 70·53; H = 8·01 per cent.

The *imide* of cyclo*heptanediacetic acid*,

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2 \end{array} \!\!>\! C \!<\!\! \begin{array}{l} CH_2\cdot CO \\ \\ CH_2\cdot CO \end{array}\!\!> NH,$$

is formed as a by-product in the hydrolysis of the dicyano-imide, and can be obtained by evaporating the ether used for extracting the acid after the latter has been removed by means of sodium carbonate solution. The solid residue crystallises extremely well from benzene, and is obtained in large, iridescent plates melting at 177—178·5°:

0·1202 gave 8·0 c.c. N_2 at 20·0° and 757·1 mm. N = 7·55.

$C_{11}H_{17}O_2N$ requires N = 7·18 per cent.

Examination of the Mother Liquors from the Original Condensation (Compound VI, p. 641).

The ethereal extract containing unchanged suberone is reduced to a small bulk by distillation on a steam-bath, using an efficient fractionating column to prevent loss of ketone. The residue in the flask is treated with a concentrated solution of sodium hydrogen sulphite, which rapidly combines with the ketone; the solid compound is isolated by filtration, purified by grinding with ether, and

yields, on decomposition with alkali, the ketone in a state of purity; about one-fifth to a quarter of the original amount is recovered in this way.

The ethereal washings are added to the filtrate from the hydrogen sulphite compound, which contains mainly cyanoacetamide, in addition to oily impurities. On prolonged keeping, a small quantity of a very sparingly soluble solid separates, and can be purified by recrystallisation from much alcohol, separating from this solvent in prisms melting at 187°:

0·1367 gave 0·3745 CO_2 and 0·1078 H_2O. C=74·71; H=8·76.

0·1581 „ 14·8 c.c. N_2 at 22·0° and 748·8 mm. N=10·40.

$C_{17}H_{24}ON_2$ requires C=74·94; H=8·89; N=10·29 per cent.

On boiling for ten minutes with concentrated hydrochloric acid, this compound is transformed into a semi-solid mass which solidifies on cooling. On crystallisation from dilute alcohol, this is obtained in small plates melting sharply at 137°. It is much more readily soluble in alcohol than the former compound, with which it is isomeric:

0·1482 gave 0·4973 CO_2 and 0·1159 H_2O. C=74·94; H=8·69.

0·1606 „ 14·6 c.c. N_2 at 21·3° and 775·2 mm. N=10·46.

These compounds are still under investigation.

In conclusion, our best thanks are due to Prof. J. F. Thorpe, F.R.S., for his interest in the course of the investigation; we are indebted to Messrs. May and Baker, Ltd., of Battersea, for having undertaken the preparation of crude suberic acid from which our suberone was prepared; and to Mr. E. A. Perren, of this College, for his help in the purification of suberic acid.

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South Kensington. [*Received, April 28th*, 1920.]

LXVIII.—*Estimation of Nitroform by Potassium Permanganate.*

By Phyllis Violet McKie.

A simple and accurate method of estimating nitroform in the presence of nitric, nitrous, and sulphuric acids when titration by alkali hydroxide (Hantzsch, *Ber.*, 1899, **32**, 628) is not applicable is found in the reduction of permanganate in acid solution (compare Orton and McKie, this vol., 283).

$$CH(NO_2)_3 + 2O_2 + H_2O = CO_2 + 3HNO_3.$$

That this equation quantitatively represents the reaction was confirmed by determining the nitric acid (by oxidation by ferrous salt in an atmosphere of carbon dioxide) produced from given quantities of nitroform and potassium permanganate. Thus it was found that 1 mole of potassium nitroform ($CK[NO_2]_3 = 189{\cdot}15$) reduced (i) 79·84, (ii) 79·96, (iii) 79·95 litres of $N/10$-permanganate, and yielded (i) 2·997, (ii) 2·990, (iii) 2·995 moles of nitric acid.

To ascertain the best procedure and to test the accuracy of the method, standard solutions were made up of the pure potassium and ammonium salts, which were prepared from pure tetranitromethane by the methods, respectively, of Hantzsch (*loc. cit.*) and Pictet and Genequand (*Ber.*, 1903, **36**, 2228), and recrystallised by slowly evaporating their aqueous (alkaline in the case of the ammonium salt) solutions at the laboratory temperature over sodium hydroxide under diminished pressure, and shielded from light.

The volumetric procedure, which was found to give the best results, is as follows. After ascertaining roughly the volume of permanganate which is required by some volume of the given nitroform solution, 25 c.c. of the latter are added to a known excess (50 c.c.) of $N/10$-permanganate acidified with 10 c.c. of 10 per cent. sulphuric acid. The mixture is then heated to 30°; after remaining for one minute at that temperature, 20 c.c. of a 2·5 per cent. solution of potassium iodide is added, and the liberated iodine titrated with $N/10$-thiosulphate, using starch-paste as indicator.

As the reaction is rather slow, both considerable excess of permanganate and the elevated temperature (30°) are essential; extension of the time or a higher temperature is not permissible, owing to a separation of manganese dioxide which then occurs. Failure to oxidise the whole of the nitroform is indicated by a persistent yellow colour after the titration of the iodine.

In nitration products, titration in the manner described results in a reduction of the permanganate equivalent both to the nitroform and to the "nitrous acid" (compare Lunge, "Sulphuric Acid and Alkali," 4th ed., 1913, **1**, i, 388). To determine the nitroform, the mixture may first be titrated, then the "nitrous acid" removed (partly) by aspiration, and the mixture again titrated. It is found that at a given temperature and with a given air current, the percentage loss of nitrous acid is independent of the initial concentration within wide limits. Thus, at 16°, with an air current of 0·1 litre per minute, it was found that 73·3 (72·8—73·9) per cent. of the nitrous acid disappears in one hour

from solutions containing nitric acid (7—8 per cent.), nitroform, and nitrous acid.

An alternative method is the destruction of the "nitrous acid" by ammonium nitrate (compare Gailhat, *J. Pharm. Chim.*, 1900, [vi], **12**, 9, and Gerlinger, *Zeitsch. angew. Chem.*, 1902, **14**, 1250, both of whom used ammonium chloride). The substitution of carbamide for the purpose leads to a small (8—10 per cent.) loss of nitroform.

To a solution of nitroform containing 0·2—0·3 gram of nitrous acid, 3 grams of ammonium nitrate are added; the mixture, which should not be alkaline, is boiled for a short time (one minute suffices), cooled to 30°, and titrated with permanganate. That the destruction of the nitrous acid is complete can be shown by potassium iodide, a reagent which is not affected rapidly by nitroform. The table illustrates the results of experiments in which nitrous acid was removed by ammonium nitrate.

$CK(NO_2)_3$. Gram.	$NaNO_2$. Gram.	$N/10$-$KMnO_4$. Nitroform. C.c.	$CK(NO_2)_3$ found. Gram.	$CK(NO_2)_3$ found. Percentage.
0·03004	0·04	12·7	0·03994	100·0
0·03004	0·04	12·67	0·02995	99·72
0·03004	0·02	12·7	0·03004	100·0
0·03004	0·02	12·69	0·03000	99·86
0·03004	0·06	12·75	0·03012	100·3
0·03004	0·06	12·72	0·03007	100·1

As an alternative, the nitroform may be distilled in a current of steam from the product (100 c.c. acidified with 15 c.c. of phosphoric acid, D 1·7), after treatment with ammonium nitrate, and the distillate titrated. About thirty minutes are required for the nitroform to pass over.

Comparisons of the above method have been made with titration by alkali of the nitroform extracted by ether (in the absence of nitrous acid), or distilled in a current of steam, and also with a method based on the precipitation by nitron (Schmidt, *Ber.*, 1919, **52**, [*B*], 400), which appeared while this investigation was in progress. The permanganate method is far more convenient, and, by comparison of the two methods, more accurate.

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Organic Chemistry.

The Electronic Constitution of Normal Carbon Chain Compounds, Saturated and Unsaturated. EUSTACE J. CUY (COUYUMDJOPOULOS) (*J. Amer. Chem. Soc.*, 1920, **42**, 503—514).—A theory of the constitution of carbon chain compounds is put forward, based on the conceptions of Hanke and Koessler (A., 1919, i, 4). Two assumptions are made: first, that carbon compounds are polar in character, and, secondly, that carbon atoms in a chain tend to assume alternately positive and negative charges, and it is shown how, by these assumptions, the alternating character of many physical properties in homologous series, for example, the melting points in the fatty acid series, can be accounted for. Further evidence in support of the hypothesis is derived from a consideration of the manner of addition of hydrogen haloids to unsaturated carbon compounds. The electronic formula for propylene, for example, is as annexed; the most hydrogenated carbon atom is electronegative; the adjacent carbon atom is electropositive, and combines with the electronegative halogen (Markovnikov's rule). A number of exceptions to this rule, Ipatiev's rule for the addition of hydrogen bromide to compounds of the type $R_2C:C:CH_2$, and the isomeric rearrangement of alkyl haloids are accounted for by the hypothesis.

$$\begin{array}{cccccc} & \mathrm{H} & & & & \\ & + & & & & \\ & - & & & & \\ \mathrm{H}+ & -\mathrm{C}- & + & \mathrm{C}^{+}_{+}\!-\!\mathrm{C}- & & +\mathrm{H} \\ & - & & -\ \ \ - & & \\ & + & & +\ \ \ + & & \\ & \mathrm{H} & & \mathrm{H}\ \ \ \mathrm{H} & & \end{array}$$

E. H. R.

Condensations of *n*-Butyl Alcohol and *n*-Butaldehyde. CHARLES WEIZMANN and STANLEY FREDERICK GARRARD (T., 1920, 117, 324—338).

The Walden Inversion. II. P. KARRER and W. KAASE (*Helv. Chim. Acta*, 1920, **3**, 244—251. Compare A., 1919, i, 570).—The action of hydrochloric acid on isobutylene oxide results in the formation of γ-chloro-α-methylpropan-β-ol, accompanied by an isomeride, which Michael considered to be β-chloro-β-methylpropan-γ-ol. There is, however, no positive evidence in favour of this view (Krassusky, A., 1907, i, 459), but confirmation of it is now brought forward. *γ-Chloro-βε-dimethylhexan-β-ol*, $CH_3·CHMe·CH_2·CHCl·CMe_2·OH$, obtained by the action of magnesium methyl iodide on ethyl α-chloro-γ-methylvalerate, is a clear oil, b. p. 77°/12 mm., with an odour resembling that of turpentine,

and has $[\alpha]_D^{14}$ $-57{\cdot}2°$ in alcohol. By treatment with potassium hydroxide, it is converted into $\beta\epsilon$-dimethylhexene-$\beta\gamma$-oxide,

$$CH_3{\cdot}CHMe{\cdot}CH_2{\cdot}\overset{O}{\overbrace{CH{\cdot}CMe_2}},$$

b. p. 134—136°, $[\alpha]_D^{16}$ $+8{\cdot}97°$ in alcohol under ordinary pressure, or 46°/17 mm., a clear liquid with a refreshing, fruity odour. It reacts instantly with cold concentrated hydrochloric acid. Although the product boils at 77°/13 mm., and has the same odour as the above chlorodimethylhexanol, it has $[\alpha]_D^{18}+14{\cdot}15°$ in alcohol, and must therefore contain a certain proportion of the isomeric β-chloro-$\beta\epsilon$-dimethylhexan-γ-ol. The possibility that the production of the mixture is due to a Walden inversion is excluded by the fact that it regenerates the above oxide when treated with potassium hydroxide. The paper concludes with comments on Clough's reply (this vol., i, 368). J. K.

Preparation of Ethylene Glycol. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 300122; from *Chem. Zentr.*, 1920, ii, 241).—Ethylene is oxidised with permanganate solution in such a manner that (1) contact of the glycol formed with the permanganate is avoided as far as possible, as, for example, by adoption of the counter-current principle, and (2) accumulation of manganese mud or other products which might retain the glycol in the reaction vessels is obviated. The yields are nearly quantitative. Technical ethylene, such as that obtained by the catalytic hydrogenation of acetylene, and therefore always containing a certain amount of impurities, of which the chief is ethane, may be advantageously used. The ethane is then obtained as by-product. H. W.

The Preparation of Halogenohydrins. JOHN READ and MARGARET MARY WILLIAMS (T., 1920, **117**, 359—362).

Preparation of Pinacone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 306304; from *Chem. Zentr.*, 1920, ii, 445). —Acetone is reduced electrolytically in acid solution in the presence of metallic salts, which inhibit its conversion into more completely reduced products, such as *iso*propyl alcohol. Salts of bismuth, mercury, manganese, nickel, antimony, silver, and iron are found to be particularly suitable for this purpose. H. W.

Preparation of Pinacone Chlorohydrin. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 317635; from *Chem. Zentr.*, 1920, ii, 445—446).—Hydrogen chloride is allowed to act on pinacone at a temperature which is above that at which the hydrogen chloride additive product is produced, and below that at which pinacolin is formed, or the additive product of pinacone and hydrogen chloride is heated to such a temperature. Pinacone chlorohydrin, a substance with a camphor-like odour, is formed quantitatively at 35—45°. H. W.

Preparation of Ethyl Ether. ELEKTRIZITÄTSWERK LONZA (D.R.-P. 317589; from *Chem. Zentr.*, 1920, ii, 445).—Acetaldehyde vapour is treated with hydrogen in the absence of oxygen and presence of a contact agent.

In previous processes, alcohol has been invariably produced by passing mixtures of acetaldehyde and hydrogen over catalysts (compare this vol., i, 134); apparently, electrolytic hydrogen has been used, which invariably contains oxygen. Only traces of ether are formed from a gaseous mixture containing even a few tenths per cent. of oxygen, whilst, in the complete absence of the latter, mixtures of ether and alcohol are produced which contain up to 15% of the former. The production of ether commences at about 90°, whilst decomposition of the acetaldehyde begins at about 170°; the temperature of the reaction chamber must therefore be maintained between 90° and 170°. H. W.

The Mechanism of the Reaction between Ethylene and Sulphur Chloride. J. B. CONANT, E. B. HARTSHORN, and G. O. RICHARDSON (*J. Amer. Chem. Soc.*, 1920, **42**, 585—595).—The formation of $\beta\beta'$-dichlorodiethyl sulphide by the action of sulphur monochloride on ethylene at 40—60° is the result of two successive reactions, which take place with different velocities. Experiments with carbon tetrachloride and trichlorodiethyl sulphide having confirmed the proportionality of molecular concentration of solute to depression of freezing point of $\beta\beta'$-dichlorodiethyl sulphide, the relationship between ethylene absorption and dichlorodiethyl sulphide formation in the above reaction was determined by the addition of samples of the reaction mixture to such quantities of the pure sulphide as to depress its freezing point from 13·9° to 5—9°. Of the following pairs of figures, the first represents the percentage of sulphide in the reaction mixture when the ethylene absorbed was a percentage of the total eventually absorbed given by the second figure: 0·0, 23·8; 25·5, 45·0; 52·6, 67·25; 70·1, 87·5; 84·9, 100·0. The first stage in the reaction therefore consists in the formation of an intermediate compound, which only reacts further with ethylene when the absorption has reached about 30%; at the stage of 60—70% absorption, the reactions proceed at about the same rate, and later the second predominates completely. An intermediate compound from sulphur dichloride can be isolated in a fairly pure condition (with sulphur and chlorine contents 1% too low and too high, respectively, for the formula $CH_2Cl\cdot CH_2\cdot SCl$) by shaking it at 0° in excess of ethylene. The resulting pale yellow liquid apparently combines with sulphur when warmed with it, because the black, oily product is completely soluble in carbon tetrachloride, and is probably a polysulphide, since by oxidation with nitric acid, sulphuric acid and an unidentified organic sulphonic acid are produced. The intermediate product also evolves hydrogen chloride slowly at 0°, rapidly at 50°, very rapidly in presence of iron or ferric chloride at 5°, and is converted into a viscid, black oil. A similar product, which

behaves very similarly, is present in sulphur monochloride which has absorbed one mol. proportion of ethylene, but the presence of some unchanged monochloride and some dichlorodiethyl sulphide prevents its isolation. Although the ethylene absorbed by sulphur monochloride amounts to 95% of that theoretically required for its complete conversion into the sulphide, only about 80% of this is actually produced, whilst only about 50% of the calculated amount of sulphur is produced (it is not precipitated, but is in colloidal solution, from which it separates slowly at the ordinary temperature and rapidly at 100°, leaving the freezing point of the disulphide unchanged). Correspondingly, a black tar, completely soluble in organic solvents, and so free from elementary sulphur, remains when the sulphide is removed from the final product by distillation under reduced pressure. This tar corresponds approximately in composition with the formula $(CH_2Cl\cdot CH_2)_2S_5$, and, in conformity with this, by oxidation with nitric acid, gives sulphuric acid and a sulphonic acid, probably $CH_2Cl\cdot CH_2\cdot SO_3H$ (compare Spring, A., 1888, 664). The tar is decomposed by steam at 200°, leaving a black residue rich in sulphur, whilst the steam removes a yellow oil, which boils under reduced pressure with decomposition, and is probably $(CH_2Cl\cdot CH_2)_2S_3$, since, on oxidation, it yields sulphuric acid and a sulphonic acid. That the tar is not a product of decomposition during distillation follows from the fact that its mixture with the requisite amount of pure dichlorodiethyl sulphide has the properties of the original crude product. J. K.

Chloromethyl Chloroformates. ANDRÉ KLING, D. FLORENTIN, A. LASSIEUR, and R. SCHMUTZ (*Ann. Chim.*, 1920, [ix], **13**, 44—59).—A more detailed account of work already published (compare this vol., i, 8, 139, 213). W. G.

Alcoholysis. II. Alcoholysis in the Absence of a Catalyst. J. J. SUDBOROUGH, N. B. BHAGVAT, and V. K. BHAGVAT (*J. Ind. Inst. Sci.*, 1918, **2**, 121—136).—A study of the alcoholysis in the absence of a catalyst of the methyl and ethyl esters of three pairs of acids, chosen so that each pair were similar in constitution, one being, however, a relatively strong acid and the other relatively weak. The results clearly indicate that esters derived from relatively strong acids enter into double decomposition with monohydric alcohols more readily than do the corresponding esters of weak acids.

Experiments made with methyl dichloroacetate and propyl alcohol confirmed these results, but in this case there was also a certain amount of replacement of the chlorine by the propyl group. W. G.

Colloid Chemical Studies of Soaps. III. Colloid Chemistry of Potassium Oleate and the Salting-out of Soaps. IV. Reaction of Soaps to Indicators. M. H. FISCHER and MARION O. HOOKER (*Chem. Eng.*, 1919, **27**, 253—257, 271—276. Compare this vol., i, 215).—In the first paper the various

theories are discussed that have been proposed to explain the salting out of soaps. The electrolytic theory which attributes the results to the neutralisation of the charge on the particles is inadequate. The authors advance the following. When small amounts of salt are added to a soap–water system the molecules of the former become hydrated and dispersed in the soap–water medium. Further addition of the salt causes not only a greater dehydration of the soap, but also an increase in the viscosity of the system due to the larger proportion of the disperse phase. When sufficient salt has been added the hydrated particles of salt touch one another and a reversal takes place, whereby the largely dehydrated soap becomes the disperse phase. As the density of the dehydrated soap is much less than that of the salt solution the former rises to the top.

In the second paper the contention is raised that a soap made from equivalent amounts of a fatty acid and a standard alkali solution is either acid, neutral, or alkaline toward an indicator, such as phenolphthalein, depending on the concentration of water in the system. A soap–water system may be water dispersed in hydrated soap or hydrated soap dispersed in water. Indicators react with the latter, but not with the former. On heating a soap gel the water may change from the disperse phase to the disperse medium. For this reason the indicator might react with the system at the higher temperature, where it could not do so with the cold gel. These facts must be borne in mind in the application of indicator methods to biochemistry. Living matter is made up of colloids containing water rather than of water containing colloids. It therefore is not always possible to determine by the use of an indicator whether living matter is acid, neutral, or basic. CHEMICAL ABSTRACTS.

β-Alkylthiolcrotonic Esters. HELMUTH SCHEIBLER and JULIUS VOSS (*Ber.*, 1920, **53**, [*B*], 379—388).—A series of β-alkylthiolcrotonic esters has been prepared by the action of sodium alkyl sulphides on the isomeric β-chlorocrotonic esters. In striking contrast to the behaviour of the corresponding free acids, it is found that the normal form is the more stable; isomerisation during the course of the reaction appears to depend not only on the mercaptan used, but also on the particular ester employed.

The β-chlorocrotonic esters are most advantageously prepared (yield, 90—95% of that theoretically possible) by converting the acids into their chlorides by means of thionyl chloride and treating the crude product of the reaction, after removal of excess of thionyl chloride, with the requisite alcohol.

Methyl β-benzylthiolcrotonate, colourless, rhombic leaflets, m. p. 69—70°, is prepared by the action of a methyl-alcoholic solution of sodium benzyl sulphide on methyl chloro*iso*crotonate or methyl chlorocrotonate or from cold methyl alcohol and β-benzylthiolcrotonyl chloride. *Ethyl β-benzylthiolcrotonate*, six-sided plates or rhombic crystals, m. p. 64·5°, is exclusively formed by the action of ethyl β-chlorocrotonate on an alcoholic solution of sodium benzyl-

sulphide; with the corresponding *iso*-ester, however, the main product is *ethyl β-benzylthiolisocrotonate*, viscous, yellow oil, b. p. 204—205°/15 mm., but a small proportion is always converted into the normal ester. Ethyl β-chloro*iso*crotonate yields a mixture of the isomeric *ethyl β-ethylthiolcrotonates*; by fractionation of the product obtained by the action of sodium ethyl sulphide on the mixture of ethyl β-chlorocrotonates it was found possible to isolate the *iso*-ester, b. p. 125—126°/14 mm., 127—129°/16 mm., and 232—236°/ordinary pressure, and the normal ester, b. p. 139—141°/16 mm. H. W.

Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. I. Preparation and Properties of Metallic Compounds of Enolic Forms of Fatty Esters. Action of Ethyl Potassioacetate on Halogenacyl Compounds. HELMUTH SCHEIBLER and JULIUS VOSS (*Ber.*, 1920, **53**, [*B*], 388—409. Compare Scheibler and Babe, A., 1916, i, 14).—The potassio-derivatives of esters which contain at least one hydrogen atom attached to the carbon atom in the α-position to the carbalkyloxy-group are readily obtained when an ethereal solution of the ester is added to the finely-divided metal which is covered with ether heated to gentle ebullition; the metal dissolves immediately with evolution of hydrogen, and the metallic derivative remains more or less completely in colloidal solution in the ether. Sodium acts less energetically, and the corresponding derivatives can frequently be only obtained in boiling benzene or toluene solution, whereby they are partly decomposed. Increase in the weight of the alkyloxy-group appears to facilitate the reaction. The ester-enolates are very unstable substances, which, however, may be preserved for several days under ether in an atmosphere of hydrogen or nitrogen. Condensation with resulting formation of brown products occurs when their suspensions or solutions in benzene or toluene are warmed, and, on subsequent acidification with dilute mineral acids, acidic products are obtained. They are immediately decomposed by water into ester and alkali hydroxide; addition of alcohol causes the separation of alkyloxide. Dry oxygen is absorbed with formation of brown products. They react with carbon dioxide to give colourless potassium salts of carboxylic acids, which are stable towards oxygen and water, but contain the carboxyl group very loosely combined. They readily undergo addition, condensation, and substitution. Of the various derivatives prepared, ethyl potassio-acetate has been most fully investigated; apart from its mode of formation, the main evidence on which the formula, CH_2:C(OK)·OEt, proposed for it rests is its action toward ethyl chloroformate. When the substances are brought together in cold ethereal solution, potassium chloride is immediately precipitated, and the primary, unpleasant-smelling product is decomposed when the solution is boiled, yielding substances with an ester-like odour; on acidification of the solution, carbon dioxide, ethyl acetate, ethyl

carbonate, and ethyl malonate are obtained, the latter in very small amount. The reactions may be represented by the schemes:

$$2CH_2{:}C(OEt){\cdot}O{\cdot}CO_2Et \longrightarrow [CH_2{:}C(OEt){\cdot}O]_2CO + Et_2CO_3;$$
$$[CH_2{:}C(OEt){\cdot}O]_2CO + H_2O \longrightarrow 2CH_3{\cdot}CO_2Et + CO_2;$$
$$[CH_2{:}C(OEt){\cdot}O]_2CO + 2KOH \longrightarrow 2CH_3{\cdot}CO_2Et + K_2CO_3.$$

The reaction just described offers a certain contrast to that observed by Bouveault and Locquin (A., 1906, i, 782), who, by the action of sodium on solutions of fatty esters in ether or benzene and decomposition of the products with water, obtained ketols; the difference is to be ascribed to the different mode of operation since, in the present instance, the experiments were performed in such a manner that the liberated hydrogen was immediately removed, whilst the French chemists worked at a lower temperature at which the reducing action of the gas could come into operation.

The following individual compounds are described: *ethyl potassioacetate*, pale yellow, amorphous, very hygroscopic powder; *methyl potassioacetate*, pale ochre-yellow; *ethyl sodioacetate*, pale reddish-yellow; *amyl sodioacetate*, yellow; *ethyl potassiopropionate*, pale yellowish-red; *ethyl potassiobutyrate*, yellow, amorphous powder; *ethyl potassiocrotonate*, ochre-coloured powder; *ethyl potassio-β-ethoxycrotonate*; *methyl potassio-β-ethylthiolcrotonate*, yellow powder, which does not absorb dry oxygen; *ethyl potassio-β-ethylthiolcrotonate*, ochre-coloured powder; *ethyl potassio-β-ethylthiol*isocrotonate resembles the preceding substance; *methyl sodio-β-benzylthiolcrotonate*, red powder; *ethyl potassio-β-benzylthiolcrotonate*, yellow; *ethyl sodio-β-benzylthiol*isocrotonate resembles the isomeric compound; *ethyl dipotassio-ββ-thiodicrotonate*, wine-red powder; *ethyl potassiocinnamate*, red powder. Ethyl acetoacetate (1 mol.) and potassium (2 atoms) yield a white product which is readily soluble in ether to a brown solution, but half of the potassium remains unchanged. Ethyl αα-diethylacetoacetate evolves hydrogen when treated with potassium, and yields a yellowish-red, pulverulent, metallic derivative, which is probably formed by enolisation of the β-carbonyl group. Benzoic ester, on the other hand, does not evolve hydrogen when treated with potassium, but slowly gives a black product, which yields acidic substances after being decomposed by water.

The action of acetyl and benzoyl chlorides on ethyl potassioacetate is fundamentally similar to that of ethyl chloroformate. When the solutions are heated, however, various condensation products are formed. The primary product obtained by the use of acetyl chloride is smoothly converted by gaseous ammonia into acetamide and ethyl acetate, $NH_3 + CH_2{:}C(OEt){\cdot}O{\cdot}COMe = CH_3{\cdot}CO{\cdot}NH_2 + CH_2{:}C(OEt){\cdot}OH[\longrightarrow CH_3{\cdot}CO_2Et]$; when, however, the product is distilled it gives alcohol, ethyl acetate, acetic acid, and acetic anhydride. Similarly, the substance formed when benzoyl chloride is employed yields alcohol, benzoic anhydride, ethyl benzoate, and benzoic acid. Alcohol and acid anhydride appear to be the primary decomposition products from which ester and acid are subsequently

formed. In addition, a highly unsaturated residue with a terpenaceous odour is obtained, which boils over a wide range of temperature and from which it has not been found possible to isolate any individual substance. H. W.

The Walden Inversion. G. W. CLOUGH (*Helv. Chim. Acta*, 1920, **3**, 233—235).—The criticisms of Karrer and Kaase (A., 1919, i, 570) are based on a misconception of the author's views; further, the conclusions as to configuration drawn by Karrer and Kaase from their experimental observations on rotatory dispersion are premature in the present state of knowledge. The author doubts the wisdom of changing the designations of ordinary malic and aspartic acids from *l* to *d*. J. K.

Preparation of Compounds of Deoxycholic Acid. HEINRICH WIELAND (D.R.-P. 317211; from *Chem. Zentr.*, 1920, ii, 447).—The acid is mixed with a hydrocarbon or other organic compound with the exception of ether and acetic acid.

Choleic acid from bile, which has hitherto been regarded as an isomeride of deoxycholic acid, is an additive product of the latter with fatty acids (palmitic, stearic, and oleic) in the proportion of eight molecules of deoxycholic acid to one molecule of fatty acid. The stable additive products (which are not dissociated in solution) of deoxycholic acid with hydrocarbons, alcohols, phenols, aldehydes, ketones, carboxylic acids, and their esters and alkaloids, which frequently contain the components in definite stoicheiometric relationship, are generally termed choleic acids, so, for example, camphorcholeic acid, phenolcholeic acid, etc. *Stearincholeic acid*, m. p. 186°, is prepared from deoxycholic acid and stearic acid dissolved in alcohol. *Naphthalenecholeic acid* [naphthalene (1 mol.) and deoxycholic acid (3 mols.)] has m. p. 182°. The choleic acids which are freely soluble in alcohol are prepared by dissolving deoxycholic acid in the molten component, allowing the product to crystallise, and removing the excess of the second component by a suitable solvent. *Phenolcholeic acid* crystallises from a small quantity of alcohol, is odourless, and yields sparingly soluble *calcium* and *barium* salts. *Benzaldehydecholeic acid*, from benzaldehyde (1 mol.) and deoxycholic acid (3 mols.), has m. p. 168°. The products are expected to find application in pharmacy. H. W.

The Enolisation of Carbonyl Compounds under the Influence of Grignard's Reagents. VINAYAK KESHAV BHAGVAT and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1919, **2**, 187—194).—Using the method described by Hibbert and Sudborough (T., 1904, **85**, 936) for the estimation of hydroxyl groups in carbon compounds by measuring the volume of methane produced by contact with an excess of magnesium methyl iodide solution, the authors have determined the enolisation produced in a number of aldehydes, ketones, and β-ketonic esters by contact with Grignard's reagents.

The results indicate that the carbonyl group in aldehydes and ketones is only enolised to a small extent, 11% being the maximum, under these conditions. In β-diketones and β-ketonic esters, how-

ever, the carbonyl group shows a very great tendency to undergo enolisation. In the case of benzoyl- and acetyl-acetone as much as 90% of the enolic form is produced. W. G.

The Vapour Pressures of Acetone. G. R. PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 47—58).—Using the statical method, the author has measured the vapour pressures of acetone over the temperature range $-50°$ to $15°$ for a sample of fermentation acetone, D_{25}^{25} 0·7909, and for a sample of commercial "extra pure" acetone, D_{25}^{25} 0·7865. W. G.

Biochemical Synthesis of some Disaccharides: Glucobioses, Galactobioses. ÉMILE BOURQUELOT (*Ann. Chim.*, 1920, [ix], **13**, 5—44).—A full account of work already published (compare A., 1913, i, 1080, 1305; 1914, i, 72, 499, 662; 1915, i, 76, 501, 940; 1916, i, 596; 1917, i, 250; 1919, i, 137, 361). W. G.

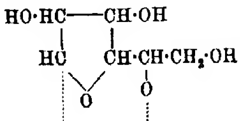
Occurrence of Melezitose in Honey. C. S. HUDSON and S. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1920, **42**, 116—125).—The occurrence of melezitose in manna from the Douglas fir of British Columbia has recently been reported (A., 1919, i, 59); the same sugar has now been found in several samples of honey. In estimating the percentage of melezitose, advantage is taken of the fact that invertase hydrolyses sucrose, but not melezitose; the change in rotation after treatment with invertase and acid, respectively, is therefore determined, or, alternatively, the reducing power may be measured after similar treatment. H. W.

Crystallography of Melezitose. EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 125—128).—The crystals of melezitose dihydrate belong to the rhombic system, and are seemingly holohedral, but no doubt bisphenoidal, $a:b:c=1·216:1:0·496$. Under the microscope, melezitose presents the form of plates and rods, in part rectangular in outline and in part terminated by faces inclined at large angles. The habit and the weak double refraction are useful in the identification of this sugar in honeys or honey dews; the dextrose which frequently separates from honeys is in rods terminated at one end by planes lying 60° apart, and rounded at the other end, and in parallel polarised light shows, at least in the centres of the grains, brilliant colours of the second order with − elongation. Sucrose can also be readily distinguished from melezitose by its much greater double refraction, α being 1·45 and γ 1·57, and by breaking into irregular fragments with oblique extinction. The refractive indices for melezitose for different wave-lengths are given in the appended table.

	Wave-length.					
Index.	450.	500.	550.	*D* 589.	600.	650.
α	1·550	1·546	1·542	1·540	1·540−	1·538
β	1·558	1·553	1·550	1·548	1·547	1·545
γ	1·561	1·556	1·552	1·550	1·549	1·547
$\gamma-\alpha$	0·011	0·010	0·010	0·010	0·009+	0·009

H. W.

Glucosides. VI. Constitution and Configuration of Glucosides. P. Karrer (*Helv. Chim. Acta*, 1920, **3**, 258—260).—Pictet has been led by his observation that the lævoglucosan obtained by distillation of starch and cellulose (A., 1918, i, 59) can be similarly obtained from a number of glucosides (this vol., i, 66) to suggest that the γ-oxide formula for glucosides should be modified. Since, however, he also found that ordinary α-glucose only yielded traces of the lævoglucosan, and the glucosides he examined were all β-compounds, it appeared to the author that spatial configuration might be the determining factor in the reaction. He confirmed this hypothesis by showing that a considerable amount of lævoglucosan is obtainable from β-glucose. Perhaps, therefore, starch and cellulose contain β-glucosidic linkings; it is possible that they contain the lævoglucosan grouping, but not necessarily so. The structure of the trimethylglucose obtained from cellulose (Denham and Woodhouse, T., 1917, 244) suggests that the glucose residues in cellulose are coupled at the points indicated (see annexed constitution).



J. K.

The Substitution of Halogens for the Amino-group in Aliphatic Amines. Chemische Fabrik Flora (Brit. Pat. 132245). —The amino-groups of aliphatic amines may be replaced by chlorine or bromine by treatment at 50—100° with a mixture of nitric acid (D 1·4) and concentrated hydrochloric or hydrobromic acid respectively. The reaction, which from the technical point of view is particularly applicable to the amino-acids, such as leucine or aspartic acid, is accompanied by vigorous evolution of nitrogen, and proceeds without appreciable formation of by-products. Instead of using a mixture of the two acids, nitric acid may be used with a chloride or bromide, or the halogen acid with a nitrate.

G. F. M.

Preparation, Crystallography, and Optical Properties of Methyl- and Ethyl-ammonium Mercuri-iodides. George S. Jamieson and Edgar T. Wherry (*J. Amer. Chem. Soc.*, 1920, **42**, 136—145).—It has been found recently by Woodward and Alsberg (unpublished work) that minute quantities of tertiary methyl- and ethyl-amines can be precipitated and detected by Mayer's reagent in the presence of primary and secondary amines provided only small quantities of the latter are present; with larger quantities, however, the latter substances also give precipitates, which are now described. All the substituted ammonium mercuri-iodides are bright yellow in colour, and are decomposed by water, with the separation of red mercuric iodide. They all dissolve readily in an excess of potassium iodide, and care is there-

fore necessary in the preparation of Mayer's reagent, which is made by dissolving exactly 45 grams of mercuric iodide and 33 grams of potassium iodide so as to make 100 c.c. of solution.

Dimethylammonium mercuri-iodide, $NH_2Me_2HgI_3$, m. p. 122°, *trimethylammonium mercuri-iodide*, m. p. 136°, *diethylammonium mercuri-iodide*, m. p. 114°, and *triethylammonium mercuri-iodide*, m. p. 77—78° or 59—60°, according to the mode of preparation, are described. Dimethylamine and diethylamine cannot be detected in this manner if present in amounts less than 20 and 4 mg. per c.c. respectively.

The refractive indices of the compounds are extremely high (1·9 to 2·0), but cannot be accurately determined by the immersion method, since these substances are decomposed more or less rapidly by all suitable liquids. The following crystallographic data are recorded: dimethylammonium mercuri-iodide, monoclinic, domatic, $a:b:c=0·9687:1:1·3406$, $\beta=78°20'$; diethylammonium mercuri-iodide, rhombic, peri-cubic, $a:b:c=1·1572:1:0·9102$; trimethylammonium mercuri-iodide, rhombic, peri-hexagonal, $a:b:c=1·7262:1:0·9569$; triethylammonium mercuri-iodide, monoclinic, peri-tetragonal, $a:b:c=1·15:1:1·08$, $\beta=62°30'$; tetramethylammonium mercuri-iodide, rhombic, peri-hexagonal, $a:b:c=0·59:1:0·52$; tetraethylammonium mercuri-iodide, tetragonal, $a:c=1:1·1577$. H. W.

The Stereochemistry of the Platinum Atom; on Relatively Asymmetric Syntheses in Inorganic Complexes. ALEXANDER P. SMIRNOV (*Helv. Chim. Acta*, 1920, **3**, 177—195).—Werner has described the preparation and resolution into optically active components of the compounds $[Pt\,en_3]X_4$ (*Vierteljahrsschrift Naturf. Ges. Zürich*, 1917, **62**, 553), and the author now describes similar experiments with the salts $[Pt\,pn_3]X_4$ (pn = propylenediamine). No isomerism conditioned by the *cis*- or *trans*-positions of the methyl groups was observed when either the racemic or one of the active forms of the diamine were used; all three series of salts closely resembled those derived from ethylenediamine, but their solubility, especially when the active forms were present, was much greater, and this at first prevented the resolution of the inactive forms. The molecular rotations of the salts derived from each of the active forms of diamine are remarkably high and of equal value, but of opposite sign, this being the same as those of the diamines themselves; for example, $[M]_D$ for

$$D_D-[Pt\ d\text{-}pn_3]Cl_4,1H_2O$$

and for $L_D-[Pt\ l\text{-}pn_3]Cl_4,1H_2O$ = 1035° and −1013° respectively. It therefore seemed possible that the members of one series were the optical antipodes of those of the other, and this was confirmed by a consideration of the molecular rotations of the plati-compounds containing either one or two molecules of propylenediamine (Tschugaev and Sokolov, A., 1909, i, 137). From these it appears that the presence of each molecule of propylenediamine carries with it a rotation of 96°. In the above instances, the observed

rotation is very much in excess of 288°, the value calculated on the basis of three molecules of diamine, and the difference represents the rotation due to the asymmetry of the complexes themselves. This difference, however, is considerably greater than that observed by Werner for the rotation of the optically active ethylenediamine salts, owing to the influence of the methyl groups. As the salts are colourless, they show no absorption in the visible spectrum or anomalous curve of rotatory dispersion, and no confirmation of the above conclusions is obtainable on optical grounds, but these are available in the case of the corresponding cobalt compounds. Thus, a comparison of the curves of molecular rotatory dispersion of $D_D-[Co\ d\text{-}pn_3]Br_3,2H_2O$ and

$$L_D-[Co\ l\text{-}pn_3]Br_3,2H_2O$$

with those of d_D and $l_D-[Co\,en_3]Br_3,2H_2O$ shows that they have the same form, with points of inversion, respectively, at $\mu\mu$ 503·5 and 492, and maxima (or minima, as the case may be) in the region $\mu\mu$ 517—527. The values for the ethylenediamine salts are throughout numerically greater than those for the propylenediamine compounds, because these are composite values representing the effect of the active complexes and that of the active propylenediamine. The latter is always opposite in sign to the rotation of the free propylenediamine (Tschugaev and Sokolov), and, as a consequence, in the region where the values for the ethylenediamine derivatives show that the effect of the complex is scarcely perceptible, a second reversal of sign takes place at $\mu\mu$ 626. Finally, the product which separated when a solution containing $[Pt\,r.\text{-}pn_3](d\text{-}C_4H_4O_6)_2$ was nucleated with

$$L_D-[Pt\,d\text{-}pn_3](d\text{-}C_4H_4O_6)_2,H_2O$$

was identical with this compound, and

$$D_D-[Pt\,l\text{-}pn_3](d\text{-}C_4H_4O_6)_2,H_2O$$

was obtained from the residual solution after treatment with potassium chloride.

In both cases, therefore, a total asymmetric synthesis has been effected, which is parallel to the formation of one rhamnohexonic acid and one mannoheptonic acid only from rhamnose and mannose (E. Fischer and others, A., 1888, 1049; 1889, 480). This phenomenon therefore extends to atoms with other spatial relationships than that of the tetrahedral carbon atom, and the internal spatial configuration of molecules associated with a central atom determines the spatial relationship of such molecules to that atom.

r.-*Platinum tripropylenediamine tetrachloride*,

$$[Pt\,pn_3]Cl_4,H_2O,$$

prepared by heating an alcoholic solution of chloroplatinic acid at 100° with *r*.-propylenediamine hydrochloride, forms a white granular, crystalline powder after crystallisation from dilute alcohol; the *bromide*, $r.\text{-}[Pt\,pn_3]Br_4$, from the chloride by double decomposition with sodium bromide, is a yellowish-white, crystalline powder; the *iodide*, $r.\text{-}[Pt\,pn_3]I_4$, from the chloride and ammonium iodide, is orange-yellow, but blackens even in the dark

the *sulphate*, *r*.-[Pt pn_3]$(SO_4)_2$, and the *nitrate*, *r*.-[Pt pn_3]$(NO_3)_4$, are obtained from the chloride and the corresponding silver salts.

l-*Platinum tripropylenediamine tetrachloride*,

$$L_D-[\text{Pt } d\text{-pn}_3]\text{Cl}_4,\text{H}_2\text{O},$$

prepared from *d*-propylenediamine, has $[M]_C -844°$, $[M]_D -1013°$, $[M]_E -1419°$ in 0·5% aqueous solution. The *bromide*,

$$L_D-[\text{Pt } d\text{-pn})_3\text{Br}_4,$$

iodide, $L_D-[\text{Pt } d\text{-pn}_3]\text{I}_4$, and *tartrate*,

$$L_D-[\text{Pt } d\text{-pn}_3](d\text{-C}_4\text{H}_4\text{O}_6)_2,\text{H}_2\text{O},$$

give very similar values for their molecular rotations.

d-*Platinum tripropylenediamine tetrachloride*,

$$D_D-[\text{Pt } l\text{-pn}_3]\text{Cl}_4,\text{H}_2\text{O},$$

has $[M]_C +839°$, $[M]$ $+1035°$, $[M]_E +1413°$ in 0·5% aqueous solution; the *bromide*, $D_D-[\text{Pt } l\text{-pn}_3]\text{Br}_4$, *iodide*, $D_D-[\text{Pt } l\text{-pn}_3]\text{I}_4$, and *tartrate*, $D_D-[\text{Pt } l\text{-pn}_3](l\text{-C}_4\text{H}_4\text{O}_6)_2,\text{H}_2\text{O}$, were also prepared.

The chloride and bromide of each of the last two series, obtained by resolution of the salts of the racemic series, agreed in their properties with the above description. From the chlorides, the respective active forms of propylenediamine were obtained by decomposition at 100° with formaldehyde solution.

Salts of the tri-*l*-propylenediaminecobalti-series have already been described (Tschugaev and Sokolov). Tri-*d*-propylenediamine-cobalt bromide, $D_D[\text{Co } d\text{-pn}_3]\text{Br}_3,2\text{H}_2\text{O}$, was prepared by heating *d*-propylenediamine with chloropentamminecobalt chloride, or 1:6-dichlorotetrapyridinecobalt chloride, or 1:6-dichlorodipropylenediaminecobalt chloride; the solution of the chloride thus obtained being treated with sodium bromide. Details are given of the values for the molecular rotations with various wave-lengths, from which the curves described above were constructed.

J. K.

Preparation of Hexamethylenetetramine. A. Sander (*Zeitsch. angew. Chem.*, 1920, **33**, 84).—The author disputes Herzog's contention (this vol., i, 292) that the formation of hexamethylenetetramine by treatment in the cold of an ammonium salt with excess of formaldehyde is confined to the carbonate. The reaction also takes place with other ammonium salts, and may be utilised for their estimation. Ammonium carbonate, however, more readily yields a pure product than other salts. W. J. W.

Synthesis of a Peptide of Aspartic Acid by means of Vegetable Enzymes. C. Ravenna (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 55—58).—Treatment of aqueous asparagine solution with pulped spinach leaves in presence of toluene for twenty days at about 25° appears to result in the formation of the dipeptide of aspartic acid, asparagylaspartic acid (compare this vol., i, 150, 151) in small proportion. Further experiments on a large scale are in progress.

T. H. P.

Compounds of Thiocyanates of certain Bivalent Metals and Hydrazine. PRIYADARANJAN RÂY and PULIN VIHARI SARKAR (T., 1920, **117**, 321—323).

Chromic Thiocyanates. NIELS BJERRUM (*Det. K. Danske. Vidensk. Selskabs Skrifter, Nat. Math.*, 1915, **7**, pp. 66; from *Chem. Zentr.*, 1920, i, 414—415).—A full account is given of the complex chromic thiocyanates and their equilibrium.

Tervalent chromium yields the following complex ions with H_2O and CNS (CNS=X), in which the water is replaced step by step by the CNS radicle: $Cr\,aq_6^{+++}$, $Cr\,aq_5X^{++}$, $Cr\,aq_4X_2^{+}$, $Cr\,aq_3X_3$, $Cr\,aq_2X_4^{-}$, $Cr\,aqX_5^{--}$, and CrX_6^{---}. The substance, $Cr\,aq_3X_3$, is a non-electrolyte. The existence of the second and third complexes could be established in solution, but the corresponding substances could not be isolated in the solid state; they are insoluble in ether. *Trithiocyanotriaquochromium* could be obtained in the crystalline condition, but not in a state of purity; in solution, it can be prepared in a much purer form. The molecular conductivity of a $0\cdot1N$-solution of the crystals is $\mu=3\cdot87$ at 0°, whilst, under similar conditions, the value $\mu=250$—300 is in general observed for a tervalent electrolyte. When dried in a vacuum, the very hygroscopic crystals retain $3\cdot2$—$3\cdot6$ H_2O, which is obviously chemically combined in the complex. The *tetrathiocyano*-complex could be obtained in the form of a dilute solution of the free acid, from which the corresponding salts were prepared, but could not be isolated in the solid state. Quinine and strychnine yielded precipitates of varying composition; quinoline salts gave an oily precipitate. The free acid is freely soluble in ether, in which the salts do not dissolve. The *pentathiocyano*-complex was isolated as the beautifully crystalline *quinoline* salt, from which the free *acid* and the *sodium* salt were prepared. It contains $1H_2O$ in complex union; the free acid is soluble in ether, but the salts are not. The *quinoline* salt (which does not contain water of constitution) and the *pyridine* salt of the hexathiocyano-complex are described. All the chromothiocyano-complexes give reddish-violet solutions in water, the shade becoming more red and deeper with increasing CNS content.

For the soluble complexes the partition-coefficient between ether and water at the ordinary temperature is: $Cr\,aq_3X_3$, *ca.* 3·6; $H[Cr\,aq_2X_4]$, *ca.* 9·4; $H_2[Cr\,aq\,X_5]$, ca. 4; $H_3[CrX_6]$, *ca.* 0·3. In the cases of the tri- and tetra-thiocyano-complexes the values for the partition-coefficient depend somewhat on the mode of preparation of the compounds, which probably points to the presence of mixtures of stereoisomerides, such as are to be expected from Werner's theory.

The velocity of decomposition of the several complexes has been measured by estimating the concentration of the CNS ions by the coloration with ferric nitrate. In aqueous solution, the stability of the hexathiocyano-complex is almost independent of the reaction of the solution. The remaining complexes become more stable in

acid solution as their CNS content diminishes, whilst the reverse is the case in alkaline solution. The trithiocyano-complex is fairly stable in ethereal solution, in which the stability of the other complexes rapidly diminishes with the CNS content. The complexes are sensitive to light.

Analytical methods for the estimation of the several complexes have been worked out. The hexa- and penta-complexes are first precipitated as quinoline salts, and their relative proportions in the precipitate are elucidated by estimation of the Cr and CNS content. The tri- and tetra-complexes are removed from the filtrate by means of ether when it is found possible to separate them by fractionation and to determine their amounts by two chromium estimations. Finally, chromium and thiocyanogen are titrimetrically estimated in the extracted aqueous solution, and the content of mono- and di-complex can then be calculated if the content of hexa-aquo-complex is known. The latter is determined by precipitation as chrome alum with potassium hydrogen sulphate and alcohol.

The chromothiocyano-complexes are slowly formed in solutions which contain the hexa-aquochrome-ion and the CNS ion. At the ordinary temperature, however, the stable state is not attained for some years. The chemical equilibrium between the various complexes and the CNS ion has been determined in aqueous solution at 50° for ten solutions. The results of chemical analysis are confirmed by measurements of the electrolytic conductivity. The affinity of the chromium atom for the CNS ion in normal solution is calculated from the equilibrium constants in the usual manner, and is found to be $+3710$ cal. for the first and -570 cal. for the last CNS group.

Graphs are given showing the relationship between the complexity and the concentration of the CNS ion, from which the equilibrium in a solution can be calculated if the concentrations of Cr and CNS are known. H. W.

The Thiocyanates of Gold and Free Thiocyanogen. Gold Chloride. NIELS BJERRUM and AAGE KIRSCHNER (*Det. K. Danske Vidensk. Selskabs Skrifter, Nat. Math.*, 1918, **8**, pp. 76; from *Chem. Zentr.*, 1920, i, 415–417).—The thiocyanates of gold have been investigated, since they are representatives of very complex and somewhat unstable salts, and permit the examination of the different stages of oxidation of a metal. The behaviour of aurithiocyanates leads to the assumption of the existence of free thiocyanogen in solution.

Potassium aurithiocyanate, $KAuX_4$ ($X=CNS$), is very sparingly soluble in water, the solubility product being 6×10^{-5} in 1·4 ionic normal solution. *Ammonium aurithiocyanate*, NH_4AuX_4, is a reddish-yellow substance prepared by the precipitation of an aqueous solution of ammonium thiocyanate with a solution of auric chloride (0·4% Au) in hydrochloric acid. *Sodium aurithiocyanate* forms ruby-red needles, solubility product 5×10^{-4} in 2·2 ionic-normal solution. *Hydrogen aurithiocyanate*, $HAuX_4,2H_2O$, forms dark red crystals and is prepared by mixing an acidified solution of

sodium thiocyanate with chloroauric acid and extracting the solution with ether. In pure solution, the aurithiocyanate is mainly present as the ion, AuX_4^-, the complexity constant of which,

$$K_X = AuX_4/Au^{+++} \times X^{-4},$$

is $10^{17.7}$ times as great as that of the $AuCl_4$ ion. It is dark reddish-brown in colour, and at $\lambda=578\,\mu\mu$ has a molar extraction-coefficient, 108. When the concentration of the thiocyano-ion is greater than 0·2, penta- and hexa-thiocyanoauri-ions are present in considerable amount, the complexity constants of which are $K_{AuX_5} = AuX_5^{=}/AuX_4 \times X = 1{\cdot}0$ and $K_{AuX_6} = AuX_6^{\equiv}/AuRh_5^{=} \times Rh = 1{\cdot}1$. The colour is darker than that of the tetra-complex, whilst the molar extinction-coefficient for the penta-complex is about 218 and for the hexa-complex about 248 for $\lambda=578\,\mu\mu$. At low concentrations of the thiocyanogen and hydrogen ions, the tetra-complex appears to undergo hydrolysis according to the scheme $AuX_4^- + H_2O = AuX_3(OH)^- + H^+ + X^-$, but even when H^+ and $Rh^- = 0{\cdot}01$ scarcely more than 20% is thus decomposed. The tetra-thiocyanoauri-ion is dissociated into dithiocyanoauri-ion and free thiocyanogen, $AuX_4^- = AuX_2^- + X_2$, the latter functioning as a colourless, composite halogen, the activity of which lies between those of bromine and iodine; it is liberated from thiocyanates by bromine, but immediately displaces iodine from iodides. It is extremely unstable and rapidly undergoes hydrolysis in aqueous solution, $3(CNS)_2 + 4H_2O = 5H^+ + 5(CNS)^- + HCN + H_2SO_4$; this final result is due to four partial processes: (1) $(CNS)_2 + H_2O \rightleftarrows H^+ + CNS^- + H(CNS)O$; (2) $2H(CNS)O \longrightarrow H^+ + CNS^- + H(CNS)O_2$; (3) $H(CNS)O + H(CNS)O_2 \longrightarrow H^+ + (CNS)^- + H(CNS)O_3$; (4) $H(CNS)O_3 + H_2O \longrightarrow HCN + H_2SO_4$. The velocity of reaction is conditioned by the slow rate of the second process, for which the following equation is valid: $d[X_2]/dt = -k'[HXO]^2 = -KX^2/[H^+]^2 \times [X^-]^2$, k being about 5 at 18°.

Hydrogen aurothiocyanate, $HAuX_2$, is prepared as an unstable oil by the reduction of hydrogen aurithiocyanate with sulphite, acidification of the solution, and extraction with ether. The corresponding *potassium* salt consists of slender, colourless needles readily soluble in alcohol, but decomposed by water. The *ammonium* salt is colourless and crystalline. The complexity constant of the AuX_2^- ion, which is present in the aqueous solution of these salts, is $10^{22.4}$ times smaller than that of the corresponding cyanogen ion. *Monamminoaurothiocyanate*, $AuNH_3X$, from ammonia and dithiocyanoauro-salts in reversible reaction, is unstable and sensitive to light.

Aurithiocyanate may be estimated in the presence of aurothiocyanate by titration with sulphite until a colourless solution results, since the latter ion is colourless. In solution, aurithiocyanate is converted into aurothiocyanate by auto-reduction in accordance with the scheme: $3AuX_4^- + 4H_2O = 3AuX_2^- + 5H^+ + 5X^- + HCN + H_2SO_4$; the presence of hydrogen and thiocyanogen ions and of aurothiocyanate retards this action, which is caused by the instability of free thiocyanogen liberated owing to dissociation of

the aurithiocyanate. The rate of reaction can be calculated from the dissociation constant of aurithiocyanate and the velocity of decomposition of thiocyanogen. A solution of aurothiocyanate dissociates into gold and aurithiocyanate: $3AuX_2^- = 2Au + AuX_4^- + 2X^-$, the equilibrium constant of which is *ca.* 33. The rate of reciprocal action increases with decreasing concentration of H- and CNS-ions. The presence of gold powder catalyses the change. The conjoint effect of auto-reduction and precipitation of gold is that solutions of gold thiocyanate gradually deposit the whole of the metal.

In hydrochloric acid solution the gold of chloroauric acid is mainly present in the form of the ion, $AuCl_4^-$, which, in pure solution, is hydrolysed as follows: $AuCl_4^- + H_2O = AuCl_3(OH)^- + H^+ + Cl^-$. The equilibrium constant is $0{\cdot}55 \times 10^{-4}$.

The authors have estimated the following normal potentials at about 18° (X=CNS): (1) $Au + 2X^- = AuX_2^- + \ominus$, 0·689 volt; (2) $AuX_2^- + 2Rh^- = AuX_4^- + 2\ominus$, 0·645 volt; (3) $Au + 4X^- = AuX_4^- + 3\ominus$, 0·660 volt; (4) $Au + 4Cl^- = AuCl_4^- + 3\ominus$, 1·001 volt; (5) $2X^- = X_2 + 2\ominus$, 0·769 volt. The value given by Abegg and Campbell for the normal potential of the gold auro-ion is untrustworthy, since when measurements of the gold electrode potential ion in concentrated nitric acid solution saturated with aurous oxide are made, it is, in reality, the oxidation potential of the nitric acid which is determined. H. W.

Isomerisation and Polymerisation of Methyl Thiocyanate. J. Gillis (*Rec. trav. Chim.*, 1920, **39**, 330—338. Compare A., 1918, i, 157).—By repeating Walden's work (compare A., 1906, ii, 336) it was found that, at 130°, the influence of different dissolved substances was variable. Except with cadmium iodide and sulphuric acid, the catalytic effect in causing isomerisation and polymerisation is a minimum. Methyl thiocyanate undergoes appreciable isomerisation at 130°, and polymerisation is also noticeable. The ebullioscopic constant of methylthiocarbimide is in agreement with the constant deduced from Trouton's law.

A study of the influence of temperature shows that isomerisation is practically a complete reaction, but it is always accompanied by some polymerisation. Foreign substances introduced into the methyl thiocyanate may have differing catalytic effects on the isomerisation and on the polymerisation. Thus cadmium iodide accelerates the former and sulphuric acid the latter. W. G.

New Method of Formation of Nitriles by Catalysis. A. Mailhe (*Compt. rend.*, 1920, **170**, 813—815).—Aliphatic or aromatic nitriles may be prepared by passing the vapours of the corresponding esters, along with ammonia, over aluminium oxide or thorium oxide at 500° (compare A., 1918, i, 105). It is now shown that the ammonia may be replaced by the vapours of primary amines, the action being $R{\cdot}CO_2Et + C_nH_{2n+1}{\cdot}NH_2 = R{\cdot}CN + EtOH + H_2O + C_nH_{2n}$. In some cases, slight secondary actions occur. W. G.

Preparation of Unsaturated Nitriles by Catalysis. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 226—229).—The method of preparation of aliphatic or aromatic nitriles, by passing the vapours of the esters of the corresponding acids, along with ammonia, over aluminium oxide at 480—500° (compare preceding abstract), can be applied to the preparation of unsaturated nitriles, such as crotononitrile, oleonitrile, elaïdonitrile, and cinnamonitrile. W. G.

An Isomeride of Potassium Ferricyanide. II. I. BELLUCCI (*Gazzetta*, 1920, **50**, i, 23—29).—Hauser and Biesalski's statement (A., 1913, i, 26) that the green isomeride of potassium ferricyanide, described by Locke and Edwards (A., 1899, i, 407, 557), and studied by Bellucci and Sabatini (A., 1911, i, 430), Piutti (A., 1912, ii, 712), and Wells (A., 1913, i, 347), consists of the red ferricyanide contaminated with a trace of Prussian-blue, is denied. T. H. P.

Observations on some Organic Compounds of Arsenic. ALEX. MCKENZIE and JOHN KERFOOT WOOD (T., 1920, 117, 406—415).

Influence of Position on the Boiling Points of Isomeric Benzene Derivatives. NEVIL VINCENT SIDGWICK (T., 1920, 117, 389—395).

Some Derivatives of *p*-Dichlorobenzene. JOYCE H. CROWELL and L. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1920, **42**, 145—152).—The investigation was undertaken with the object of finding a method of utilising the considerable amounts of *p*-dichlorobenzene which are formed as by-products in the technical production of chlorobenzene.

p-Dichlorobenzenesulphonic acid is most conveniently prepared (yield, 85—90%) by heating *p*-dichlorobenzene with sulphuric acid containing 10—12% of sulphur trioxide at 140—150°; 2:2′:5:5′-*tetrachlorodiphenylsulphone*, colourless, diamond-shaped crystals, m. p. 179°, is also formed. 2:5-Dichloro-4-nitrobenzene cannot be conveniently sulphonated, since reaction does not occur below 150°, whilst, above this temperature, violent decomposition with almost complete decomposition occurs. 2:5-*Dichloro-4-nitrobenzenesulphonic acid*, flat, yellow, very hygroscopic needles, m. p. about 150°, can, however, be obtained by the action of fuming nitric acid (D 1·6) alone or in the presence of concentrated sulphuric acid on *p*-dichlorobenzenesulphonic acid (the *sodium*, *potassium*, *ammonium*, and *barium* salts are described). The constitution of the acid is deduced from the reduction of its sodium salt to the corresponding *amino*-compound (the *acetyl* derivative of which was prepared) and oxidation of the latter to 2:5-dichlorobenzoquinone. Reduction of an alkaline or faintly acid solution of the sodium salt of the nitrosulphonic acid yielded *sodium* 2:2′:5:5′-*tetrachloroazobenzene*-4:4′-*disulphonate*. H. W.

Benzenesulphonitroamide, Toluene-4-sulphonitroamide, 2-Nitrotoluene-4-sulphonitroamide and some of their Salts. Bruce Reid Matthews (*J. Physical Chem.*, 1920, **24**, 108—119).—A number of metallic salts of benzenesulphonitroamide, toluene-4-sulphonitroamide, and 2-nitrotoluene-4-sulphonitroamide have been prepared and described. *Ammonium benzenesulphonitroamide*, $C_6H_5\cdot SO_2\cdot N(NO_2)\cdot NH_4$, is formed by neutralising the free nitroamide with aqueous ammonia, and forms fine, yellow prisms; the corresponding *sodium*, colourless crystals; *calcium*, *barium*, *strontium*, *lithium*, *silver*, *copper*, and *nickel* salts are described, and also deep blue needles of the composition

$$(C_6H_5\cdot SO_2\cdot N\cdot NO_2)_2Cu,4NH_3.$$

Strychnine benzenesulphonitroamide, $C_6H_5\cdot SO_2\cdot N_2O_2H,C_{21}H_{22}N_2O_2$, is precipitated on adding strychnine nitrate to a hot aqueous solution of the ammonium salt.

Nitration of *p*-toluenesulphonamide with nitric acid (D 1·42—1·48) gives a mixture of p-*toluenesulphonnitroamide*, $C_6H_4Me\cdot SO_2\cdot NH\cdot NO_2$, and 2-nitrotoluene-4-sulphonitroamide, from which the former is extracted with ether; the residue obtained on evaporation of the ethereal solution, when recrystallised from toluene, gave a colourless, crystalline product, m. p. 110°. The *ammonium*, *potassium*, *barium*, *silver*, and *copper* salts are described. When silver oxide is added to an aqueous solution of the nitroamide, grey-coloured needles of the composition $C_6H_4Me\cdot SO_2\cdot NAg\cdot NO_2,2NH_3$, and a similar *copper* compound, $(C_6H_4Me\cdot SO_2\cdot N[NO_2])_2Cu,4NH_3$, can be prepared. 2-*Nitrotoluene*-4-*sulphonitroamide*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot NO_2$, is obtained in the process described; nitric acid (D 1·48—1·50) being employed. It forms pale yellow needles, m. p. 118·5°. The *potassium*, *copper*, *silver*, *nickel*, and *manganese* salts are described, and also *silver* and *copper* salts containing $2NH_3$ and $5NH_3$ respectively. Practically all the salts described are very soluble in liquid ammonia.

J. F. S.

Preparation of αβ-Dibromotetrahydronaphthalene and of Δ¹-Dihydronaphthalene. Julius von Braun (D.R.-P., 316218; from *Chem. Zentr.*, 1920, ii, 241).—Tetrahydronaphthalene is treated with the calculated quantity of bromine at 100—140°, and the dibromotetrahydronaphthalene so produced is treated, if desired, with magnesium (1 atom) in the presence of ether or with tin (rather more than 1 atom) in the presence of alcohol. *αβ-Dibromotetrahydronaphthalene* has m. p. 69°; Δ^1-*dihydronaphthalene* has b. p. 85°/15 mm., m. p. −8°, $a_D^{21\cdot 50}$ 0·9963, and is quantitatively transformed by bromine into the dibromide.

H. W.

Some Nitro-derivatives of Dimethylaniline. J. Smit (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 523—525).—In the nitration of 3:4-dinitrodimethylaniline, if the nitric acid contains much nitrous acid, or if the action proceeds for a long time, or if the temperature rises above 20°, nitroso-compounds are obtained

as well as 3:4:6- and 2:3:4-trinitrodimethylanilines. The author has isolated 3 : 4-*dinitrophenylmethylnitrosoamine*, m. p. 108—109°, and 3:4:6-*trinitrophenylmethylnitrosoamine*, m. p. 201°.

By the nitration of 3:6-dinitrodimethylaniline, in addition to the 3:4:6-trinitro-derivative, a small amount of 3:6-*dinitrophenylmethylnitrosoamine*, m. p. 132°, is obtained. In this nitration, the effect of nitrous acid on the reaction velocity is very great, and if the temperature of the reaction is perceptibly higher than the ordinary temperature, the only final product is 3:4:6-trinitrophenylmethylnitrosoamine. W. G.

Catalytic Decomposition of Schiff's Bases. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 229—234. Compare A., 1919, i, 395).—When Schiff's bases are passed alone over reduced nickel at 420—430°, a change first occurs which is similar to that which was found to occur during the catalytic hydrogenation (*loc. cit.*), $RCH\colon NR' + 2H_2 = R\cdot CH_3 + R'NH_2$, the hydrogen being formed by the partial destruction of the group $R\cdot CH\colon$. In the second place, nitriles were formed, thus: $RCH\colon NR' = RCN + R'H$, this being, however, the less important change. W. G.

The Constitution of Capsaicin, the Pungent Principle of Capsicum. II. E. K. NELSON (*J. Amer. Chem. Soc.*, 1920, **42**, 597—599. Compare A., 1919, i, 543).—Octovanillylamide (this vol., i, 154), like capsaicin, is very stable towards alkalis, and is somewhat soluble in concentrated hydrochloric acid; also, free ammonia is easily liberated from free vanillylamine when it is boiled with water or solutions of alkaline carbonates, thus explaining its observation by Lapworth and Royle during the alkaline reduction of capsaicin (T., 1919, **115**, 1109). The objections of these workers to the formulation of capsaicin as decenovanillylamide thus lose their force, and the author has now confirmed this formula by the regeneration of capsaicin from decenoyl chloride (obtained from the decenoic acid produced from capsaicin) and vanillylamine.

Indefinite results have been obtained from the oxidation of decenoic acid by chromic acid. By fusion with potassium hydroxide, acetic acid and an octoic acid, b. p. 240—245°, with a branched carbon chain, are produced. The *silver octoate*, $C_8H_{15}O_2Ag$, is sparingly soluble in water. J. K.

Influence of the Sulphonation of the Phenol on the Yields of Picric Acid. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 195—199).—The yield of picric acid depends on the relative proportions of phenolsulphonic acid and phenoldisulphonic acid in the products of sulphonation of the phenol, the yields being much higher from the disulphonic acid. The maximum yield of phenoldisulphonic acid is obtained by carrying out the sulphonation for half an hour to one hour at 100° with five parts of 93% sulphuric acid to one part of phenol. W. G.

The Identification of Phenols. II. JAMES A. LYMAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 615—619. Compare A., 1917, i, 333).—*p*-Nitrobenzyl ethers have been prepared from a number of phenols. It is advisable to employ as solvents for the etherification of esters of salicylic acid the respective alcohols from which they are derived, and to avoid excess of alkali; otherwise interchange of the alkyl groups of the alcohol and of the ester takes place to a certain extent (compare Pardee and Reid, *J. Ind. Eng. Chem.*, 1920, **12**, 129). The p-*nitrobenzyl ethers* of the following phenols had the melting points indicated: *o*-nitrophenol, 130°; *p*-nitrophenol, 187·4°; 2:4-dinitrophenol, 248°; *o*-chlorophenol, 100°; *p*-chlorophenol, 101·3°; 2:4:6-tribromophenol, 163·5°; guaiacol, 63·6°; α-naphthol, 140°; β-naphthol, 106·5°; salol, 87°; methyl salicylate, 128·2°; ethyl salicylate, 125°; butyl salicylate, 92°; *o*-tolyl salicylate, 142·5°; *m*-tolyl salicylate, 118°. J. K.

A Comparison of the Activity of certain Unsaturated Groups with the Activity of the Allyl Group in certain Ethers. S. G. POWELL and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 646—658).—A comparison of various unsaturated ethers with phenyl allyl ethers in respect of the rearrangement of the latter into *o*-allylphenols. Of compounds containing, like the allyl derivatives, an unsaturated linking in the βγ-position to the oxygen atom, phenyl and *p*-bromophenyl propargyl ethers do not yield phenolic compounds when boiled, but suffer complete decomposition; phenoxyacetonitrile was decomposed to some extent when boiled, whilst a tarry product resulted from its *p*-methyl derivative, which, however, gave a little *p*-cresol when its solution in amyl ether was boiled; the chief products of decomposition of the benzyl ethers were not diphenylmethane, but benzene, derivatives, and their *p*-nitro- and *p*-bromo-derivatives suffered more or less profound decomposition. Contrary to the statement of D.R.-P. 268099, phenyl and *p*-tolyl vinyl ethers do not suffer rearrangement, but decompose when heated, yielding phenol and *p*-cresol. δ-Phenoxy-Δ^{α}-butene, ε-phenoxy-Δ^{β}-pentene, and its β-methyl derivatives were all remarkably stable, and suffered neither rearrangement nor decomposition when boiled.

Phenyl vinyl ether, $CH_2\colon CH\cdot OPh$, from phenyl β-bromoethyl ether, b. p. 155—156°; p-*tolyl vinyl ether*, $C_6H_4Me\cdot O\cdot CH\colon CH_2$, similarly prepared, with a pleasant odour, has b. p. 177—180°; n_D^{30} 1·513; D_{25}^{30} 0·975; β-p-*bromophenoxyethyltrimethylammonium bromide*, $C_6H_4Br\cdot O\cdot CH_2\cdot CH_2\cdot NMe_3Br$, white crystals, from *p*-bromophenyl β-bromoethyl ether and trimethylamine. γ-*Phenoxypropylmethylcarbinol*, $OPh\cdot[CH_2]_3\cdot CHMe\cdot OH$, prepared by reduction of γ-phenoxypropyl methyl ketone, is a viscous oil, having b. p. 163°/20 mm., n_D^{25} 1·5123, D_{25}^{31} 1·025; by treatment with phosphorus tribromide; β-*bromo*-ε-*phenoxypentane*, $OPh\cdot[CH_2]_4\cdot CHMeBr$, is obtained. It is an oil, b. p. 172°/28 mm., with n_D^{30} 1·529, D_{25}^{30} 1·258, and with alcoholic potash gives ε-phenoxy-Δ^{β}-pentene. ε-*Phenoxy*-β-*methyl*-Δ^{β}-*pentene*,

$$OPh\cdot[CH_2]_2\cdot CH\colon CMe_2,$$

b. p. 241°/745 mm., n_D^{30} 1·505, is prepared by fractionation of the product of the action of magnesium methyl iodide on ethyl γ-phenoxy-butyrate. Phenyl β-bromoallyl ether, $OPh\cdot CH_2\cdot CBr\colon CH_2$, for the preparation of phenyl propargyl ether, is best obtained from sodium phenoxide and tribromohydrin. Similarly, p-*bromophenyl β-bromo-allyl ether*, $C_6H_4Br\cdot OCH_2\cdot CBr\colon CH_2$, is prepared from sodium *p*-bromo phenoxide as an oil, b. p. 171°/22 mm., n_D^{22} 1·587, D_{25}^{22} 1·719; p-*bromo-phenyl propargyl ether*, $C_6H_4Br\cdot O\cdot CH_2\cdot C\colon CH$, has b. p. 144°/24 mm., n_D^{30} 1·567, and D_{25}^{30} 1·468; p-*bromophenoxyacetamide*,

$$C_6H_4Br\cdot O\cdot CH_2\cdot CO\cdot NH_2,$$

forms needles, m. p. 148—149°; p-*methoxyphenyl* p-*nitrobenzyl ether*, $C_{14}H_{13}O_4N$, forms yellow needles, m. p. 88°; p-*bromophenyl* p-*nitro-benzyl ether*, $C_{13}H_{10}O_3NBr$, yellow needles, m. p. 112°; 2:4-*dibromo-phenyl* p-*nitrobenzyl ether*, $C_{13}H_9O_3NBr_2$, yellow needles, m. p. 161°.

J. K.

Preparation of Derivatives of *N*-Acylated-*p*-aminophenols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 316902; from *Chem. Zentr.*, 1920, ii, 374).—*N*-Acyl derivatives of *p*-amino-phenols are caused to react with α-bromo-α-ethylbutyrylcarbimide. Thus, the *α-bromo-α-ethylbutyrylurethane* of p-*acetylaminophenol*, $CEt_2Br\cdot CO\cdot NH\cdot CO_2\cdot C_6H_4\cdot NHAc$ (from bromoethylbutyrylcarb-imide and a suspension of *p*-acetylaminophenol in acetone), forms small, colourless, shining leaflets, m. p. 144°. The *α-bromo-α-ethylbutyrylcarbamic ester* of p-*hydroxyphenylcarbamide*, colour-less crystals, has m. p. 187°. The products exhibit marked anti-pyretic and antineuralgic, and distinct sedative and hypnotic action.

H. W.

Phenoltrisulphonic Acid and its Transformation into Picric Acid. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 199—204).—By the sulphonation of phenol with ten times its weight of sulphuric acid containing 20% of sulphur trioxide, a mixture of phenol-di- and -tri-sulphonic cids is obtained, which contains 80% of the trisulphonic acid. On nitration, the tri-sulphonic acid gives a yield of picric acid equivalent to 90% of theory. Thus, in the nitration of the phenolsulphonic acids, the yield of picric acid increases from the mono- up to the tri-sulphonic acid. The ionisation of these acids increases in the same order. Phenoltrisulphonic acid gives two *barium* salts,

$$[OH\cdot C_6H_2(SO_3)_3]_2Ba_3,2H_2O$$

and $C_6H_2{<}^{\text{—O—}}_{(SO_3)_3}{>}Ba_2$, and a *sodium* salt,

$$OH\cdot C_6H_2(SO_3Na)_3,3H_2O.$$

The barium salt is only very sparingly soluble in water, but barium sulphate may be washed free from it by 5% hydrochloric acid.

W. G.

The Hydrolysis of Naphthyl Ethers. GOPAL BALKRISHN KOLHATKAR (*J. Ind. Inst. Sci.*, 1919, **2**, 179—186).—β-Naphthyl

ethers are much more readily hydrolysed by hydrochloric acid than the corresponding α-naphthyl ethers, whilst the corresponding phenyl ethers are only decomposed to a very slight extent under similar conditions. β-Naphthyl methyl ether is more readily hydrolysed than β-naphthyl ethyl ether. The amount of ether hydrolysed is practically independent of the amount of ether present, but is approximately proportional to the volume of acid present, and the time of the reaction, and is also influenced by the concentration of the acid. W. G.

Preparation of Tetrahydro-β-naphthyl Mercaptan. GEORG SCHROETER and WALTHER SCHRAUTH (D.R.-P. 299604; from *Chem. Zentr.*, 1920, ii, 447).—Tetrahydronaphthalene is converted by chlorosulphonic acid into tetrahydronaphthalene-β-sulphonyl chloride, which is then treated with reducing agents. The *sulphonyl chloride* has m. p. 55—56°, b. p. 194—195°/14 mm., and is converted by ammonia into *tetrahydronaphthalene-β-sulphonamide*, m. p. 134—135°, and by potassium hydroxide solution (50%) into the crystalline potassium tetrahydronaphthalene-β-sulphonate. The sulphonyl chloride is reduced by zinc dust and sulphuric or hydrochloric acid to *tetrahydro-β-naphthylmercaptan*, b. p. 153—155°/26 mm., which has only a faint odour of mercaptan and yields a colourless, well-crystallised mercury salt. It is converted by methyl sulphate and alkali into the corresponding *methyl ether*, colourless, aromatic oil, b. p. 151°/14 mm. *Tetrahydronaphthylthiolacetic acid*, $C_{10}H_{11}\cdot S\cdot CH_2\cdot CO_2H$, m. p. 133—135°, is formed by the action of chloroacetic acid on a solution of the thiol in sodium hydroxide, and subsequent addition of acid. An ammoniacal solution of the mercaptan is oxidised by air to *bistetrahydronaphthyl disulphide*, $(C_{10}H_{11})_2S_2$, m. p. 87—89°. The "thionaphthol" is designed for the preparation of drugs, disinfectants, dyes, and explosives. H. W.

1:2:2:3-Tetramethyl*cyclo*pentane-1-carbinol and its Derivatives. H. RUPE and P. LÄUGER (*Helv. Chim. Acta*, 1920, **3**, 272—298).—The purposes of experimental stereochemistry demand a primary alcohol, of considerable optical activity, and easily convertible into stable esters, including those of the halogen acids. Myrtenol fulfils these requirements (A., 1915, ii, 717; Zäslin, *Diss.*, Basel, 1915), but is not easily accessible. Camphylcarbinol, otherwise suitable, is too readily dehydrated (A., 1919, i, 29). The authors have therefore studied anew the reduction of the carboxyl group of campholic acid by the method of Bouveault and Blanc, these workers having obtained very small yields in this case (A., 1904, i, 642). Apparently the first stage of such reductions consists in the addition of hydrogen with the formation of a hydroderivative, because the yields in the present case gradually increase with the degree of unsaturation of the residue of the hydroxy-compound from which the ester is derived. Thus the ethyl, the *iso*butyl, the *iso*amyl, the β-naphthyl, and the phenyl esters respectively give yields of 10—15%, 22%, 25%, 64%, and 94—96%.

β-Naphthyl campholate, $C_9H_{17}\cdot CO\cdot O\cdot C_{10}H_7$, silky leaflets, m. p. 70°, is obtained from campholic chloride and either β-naphthol or its sodium salt. Phenyl campholate, prepared in a similar way, is a liquid, b. p. 163°/10 mm. 1:2:2:3-*Tetramethyl*cyclo*pentane*-1-*carbinol*, $C_9H_{17}\cdot CH_2\cdot OH$, prepared by reduction of phenyl campholate under carefully regulated conditions, for which the original should be consulted, is a waxy mass, m. p. 64°, b. p. 96—96·5°/10 mm., with a disagreeably penetrating odour, reminiscent of that of fenchyl alcohol; in benzene, it has $[\alpha]_C^{20}$ +53·36°; $[\alpha]_D^{20}$ +67·18°; $[\alpha]_{Hg(\lambda=546\cdot3)}^{20}$ +79·42°; $[\alpha]_F^{20}$ +102·74°. The *benzoate*,

$C_9H_{17}\cdot CH_2\cdot O\cdot CO\cdot C_6H_5$,

is a viscid, colourless oil, almost odourless, b. p. 186°/12 mm. The corresponding aldehyde may be obtained from the alcohol by direct oxidation, or by Bouveault's catalytic process with copper, but the yields are poor. Better results are obtained by Merling's process (A., 1908, i, 653), which involves the following series of reactions. Campholic chloride is converted into the *anilide*, $C_9H_{17}\cdot CO\cdot NHPh$, leaflets, m. p. 93°. The crude phenyliminochloride, obtained by treatment of the anilide with phosphorus pentachloride, reacts vigorously with aniline, with the production of the *diphenylamidine*, $C_9H_{17}\cdot C(:NPh)\cdot NHPh$, leaflets, m. p. 211°; this compound, by reduction in alcoholic solution with sodium, furnishes 1:2:2:3-*tetramethyl*cyclo*pentane*-1-*diphenylmethylenediamine*,

$C_9H_{17}\cdot CH(NHPh)_2$,

leaflets, m. p. 76—77°. This product, in its crude condition, after removal of impurities volatile in steam, is hydrolysed by the addition of sulphuric acid and continuing the steam distillation. The yield is 45—55%. 1:2:2:3-*Tetramethyl*cyclo*pentane*-1-*aldehyde*, $C_9H_{17}\cdot CHO$, m. p. 37—38°, b. p. 73—74°/8 mm., resembles camphor in appearance, and has a somewhat disagreeable and penetrating odour. It has a burning taste. In alcoholic solution it slowly reduces Fehling's solution. In benzene, $[\alpha]_C^{20}$ +68·48°; $[\alpha]_D^{20}$ +89·26°; $[\alpha]_{Hg}^{20}$ +108·00°; $[\alpha]_F^{20}$ +148·65°. It is characterised by its *semicarbazone*, fine needles, m. p. 220—221° (decomp.), its *oxime*, m. p. 27—28°, b. p. 116·5—117°/8 mm., its *phenylhydrazone*, a yellow oil, b. p. 189—190°/8 mm., easily decomposed even at ordinary temperatures; its p-*nitrophenylhydrazone*, yellow leaflets, m. p. 145°; and its p-*bromophenylhydrazone*, red leaflets, m. p. 145—146°. *Ethyl β-hydroxy*-1:2:2:3-*tetramethyl*cyclo*pentane*-1-*propionate*, $C_9H_{17}\cdot CH(OH)\cdot CH_2\cdot CO_2Et$, from the aldehyde, ethyl bromoacetate, and zinc, is a yellow oil, b. p. 151—152°/10 mm. or 264°/730 mm.; its *acetyl* derivative, $C_9H_{17}\cdot CH(O\cdot Ac)\cdot CH_2\cdot CO_2Et$, is a colourless, viscid oil, b. p. 165—167°/13 mm. *β-Hydroxy*-1:2:2:3-*tetramethyl*cyclo*pentane*-1-*propionic acid*, $C_9H_{17}\cdot CH(OH)\cdot CH_2\cdot CO_2H$, prepared from the ester by hydrolysis with alcoholic potash, forms leaflets, m. p. 79·5—80° (decomp. 140°), but can be distilled almost without decomposition at 191—193°/10 mm. By dehydration with acetic anhydride it furnishes 1:2:2:3-*tetramethyl*cyclo*pentane*-1-*acrylic acid*, $C_9H_{17}\cdot CH:CH\cdot CO_2H$, long needles, m. p. 101°; this compound may also be obtained by hydro-

lysis of the above acetyl derivative, or by distilling under reduced pressure *ethyl β-bromo-*1 : 2 : 2 : 3-*tetramethyl*cyclo*pentane*-1-*propionate*, $C_9H_{17}\cdot CHBr\cdot CH_2\cdot CO_2Et$, a yellow oil, produced by the action of phosphorus tribromide on the hydroxy-ester. The acrylic acid is sparingly soluble in water, but readily in organic solvents; in benzene, $[\alpha]_C^{20}$ + 52·06°; $[\alpha]_D^{20}$ + 66·82°; $[\alpha]_{Hg}^{20}$ + 79·90°; $[\alpha]_F^{20}$ +107·39°. The *methyl* ester, $C_{13}H_{22}O_2$, is an oil, b. p. 131—132°/12 mm.; the *chloride*, $C_{12}H_{19}OCl$, an oil, b. p. 139°/13 mm.; the *ethyl* ester, $C_{14}H_{24}O_2$, an oil, b. p. 149°/12 mm., has $[\alpha]_C^{20}$ +44·91°; $[\alpha]_D^{20}$ +57·51°, $[\alpha]_{Hg}^{20}$ +68·80°, $[\alpha]_F^{20}$ +91·93°, and in benzene the values are +44·47°, 57·11°, 68·19°, and 91·60°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentane*-1-*propionic acid*, $C_9H_{17}\cdot CH_2\cdot CH_2\cdot CO_2H$, is prepared by reduction of the acrylic acid in aqueous alcoholic solution in presence of a 40% nickel catalyst (A., 1919, i, 29); it crystallises in large, thin leaflets, m. p. 89·5—90°, and in benzene has $[\alpha]_C^{20}$ +38·21°, $[\alpha]_D^{20}$ +48·38°, $[\alpha]_{Hg}^{20}$ +57·20°, $[\alpha]_F^{20}$ +75·29°; the *magnesium* salt, $[C_{12}H_{21}O_2]_2Mg$, forms leaflets; the *chloride*, $C_{12}H_{21}OCl$, is an oil, b. p. 129°/12 mm.; the *ethyl* ester, $C_{14}H_{26}O_2$, boils at 138°/12 mm. and has $[\alpha]_C^{20}$ +32·32°; $[\alpha]_D^{20}$ +40·95°; $[\alpha]_{Hg}^{20}$ +48·59°; $[\alpha]_F^{20}$ +63·15°, whilst in benzene the values are +32·94°, 41·66°, 49·14°, and 64·54°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentylmethylcarbinol*, $C_9H_{17}\cdot CHMe\cdot OH$, from the above aldehyde and magnesium methyl iodide, is a clear liquid, b. p. 96—98°/11 mm., with a faint odour of camphor; on oxidation it yields 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone, b. p. 96—102°/12 mm. (Rupe and Kloppenburg, A., 1919, i, 539; Meerwein, A., 1919, i, 162). *Phenyl* 1 : 2 : 2 : 3-*tetramethyl*cyclo*pentylcarbinol*, $C_9H_{17}\cdot CHPh\cdot OH$, m. p. 55°, b. p. 172—174°/11 mm., could not be oxidised to the ketone. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentylstyrene*, $C_9H_{17}\cdot CH\colon CHPh$, is obtained by boiling the crude condensation product from magnesium benzyl chloride and the above aldehyde with acetic anhydride, and forms leaflets with a blue fluorescence, m. p. 51°, b. p. 146—149°/11 mm. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentylbenzylcarbinyl acetate*,

$$C_9H_{17}\cdot CH(OAc)\cdot CH_2\cdot C_6H_5,$$

needles, m. p. 81—82°, b. p. 189—192°/11 mm., is also produced in the reaction.

J. K.

Arbusterol and its Derivatives. GIOVANNI SANI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 59—61).—*Arbusterol*,

$$C_{26}H_{43}\cdot OH,H_2O,$$

isolated from the oil of *Arbutus unedo* seeds, crystallises in aggregates of silky, white needles, resembling bits of straw, m. p. 129°, $[\alpha]_D^{15}$ −15·33°, its specific rotation being thus widely different from those of other phytosterols. In chloroform solution it gives with sulphuric acid a cherry-red coloration, changing to dirty violet with a purple reflexion, whilst the acid becomes at first yellow and later brown, with a green fluorescence. Its *benzoyl* derivative, $C_{26}H_{43}\cdot OBz$, forms shining, elongated, rectangular scales, m. p. 137°, and its *acetyl* derivative, $C_{26}H_{43}\cdot OAc$, crystals, m. p. 110°. The pro-

portions of halogens fixed by arbusterol differ from those fixed by other cholesterols, and are being further investigated. T. H. P.

Volatility in Steam: Benzoic Acid and its Derivatives. NEVIL VINCENT SIDGWICK (T., 1920, **117**, 396—406).

The Use of Oxalyl Chloride and Bromide for Producing Acid Chlorides, Acid Bromides, or Acid Anhydrides. III. ROGER ADAMS and L. H. ULICH (*J. Amer. Chem. Soc.*, 1920, **42**, 599—611).—When the method of preparation of aromatic anhydrides from 1 mol. of oxalyl chloride and 2 mols. of acid (A., 1918, i, 165) is applied to *m*- or *p*-nitro-, 3:5-dinitro-, or 2:4:6-trinitro-benzoic acid, mixed anhydrides, very stable towards excess of chloride, are obtained, and these, except in the case of the last compound, when melted give the simple anhydrides. Probably, therefore, in general the course of the reaction is expressed as follows: $2RCO_2H + (COCl)_2 \longrightarrow 2HCl + (R{\cdot}CO_2{\cdot}CO)_2 \longrightarrow (R{\cdot}CO)_2O + CO_2$. Less favourable results are obtained with aliphatic acids than with aromatic compounds, some acid being unchanged, and some acid chloride being produced. Acid chlorides may be prepared smoothly and in good yield by boiling acid anhydrides, including those of the nitro compounds above, with 1·5—2·5 mols. of oxalyl chloride alone or in presence of benzene for two hours; the anhydrides may be replaced by aromatic or aliphatic acids themselves, but in this case the nitrobenzoic acids only give the mixed anhydrides. Arsenic trichloride and chromyl chloride were also successfully prepared from their oxides by this method. Either anhydrides or chlorides are, however, better prepared from the sodium salts of the acids and 1 or 1—1·5 mols. respectively of oxalyl chloride in benzene solution. Possibly, in this case, mixed anhydrides are not intermediate products, because the nitrobenzoic acids do not exhibit the exceptional behaviour previously noted. Oxalyl bromide behaves in a similar manner to the chloride; better yields of acid bromides were obtained than with phosphorus pentabromide.

Excellent yields of benzanilide, anisanilide, and *p*-toluanilide were obtained from ethereal solutions of the appropriate ketoximes on adding 0·75 mol. oxalyl chloride, which therefore promotes the Beckmann rearrangement very effectively.

p-*Nitrobenzoic oxalic anhydride*, $C_2O_2(O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2)_2$, yellow crystals, which melt and decompose at 169—170°.

2:4:6-*Trinitrobenzoic oxalic anhydride*,

$$C_2O_2[O{\cdot}CO{\cdot}C_6H_2(NO_2)_3]_2,$$

yellow crystals, melts and decomposes at 228—230°, but, unlike the other anhydrides of this type, furnishes 1:3:5-trinitrobenzene, and with sodium carbonate solution easily gives sodium trinitrobenzoate.

o-*Chlorobenzoyl bromide*, $C_6H_4Cl{\cdot}COBr$, has b. p. 143—145°/37 mm.; m-*chlorobenzoyl bromide*, b. p. 143—147°/40 mm.; p-*chlorobenzoyl bromide*, b. p. 141—143°/27 mm.; *o*-bromobenzoyl bromide, b. p. 166—168°/18 mm.; p-*bromobenzoyl bromide*, b. p. 135—137°/18 mm.; p-*iodobenzoyl bromide*, m. p. 54—55°, rapidly

darkens; o-*toluoyl bromide*, b. p. 133—136°/37 mm.; m-*toluoyl bromide*, b. p. 136—137°/52 mm.; p-*toluoyl bromide*, b. p. 145—149°/42 mm.; p-*methoxybenzoyl bromide*, b. p. 183—186°/27 mm.; m-*nitrobenzoyl bromide*, m. p. 42—43°, b. p. 165—167°/18 mm.; p-*nitrobenzoyl bromide*, m. p. 63—64°; 3:5-*dinitrobenzoyl bromide*, m. p. 59—60°; *cinnamyl bromide*, m. p. 47—48°, b. p. 180—184°/40 mm.; *phenylacetyl bromide*, b. p. 150—155°/50 mm.

J. K.

Alcoholysis. III. The Alcoholysis of Aromatic Esters and the Inhibiting Influence of Ortho-substituents. J. J. SUDBOROUGH and D. D. KARVÉ (*J. Ind. Inst. Sci.*, 1919, **3**, 1—14. Compare this vol., i, 364).—The results obtained with a large number of esters of aromatic acids indicate quite clearly that sodium alkyloxides or hydrochloric acid are excellent catalysts for the alcoholysis of these esters. An ethyl ester may readily be converted into the corresponding methyl ester by dissolving it in ten times its weight of methyl alcohol, adding a small piece of sodium, and warming for ten minutes. Two substituents in ortho-positions to the ester group completely inhibit the change. The following new esters have been prepared and characterised.

Ethyl 3:5-*dibromobenzoate*, m. p. 51°, is obtained by eliminating the amino-group from *ethyl* 3:5-*dibromo*-4-*aminobenzoate*, m. p. 108°, which is prepared by brominating ethyl *p*-aminobenzoate in dilute sulphuric acid solution. *Methyl* 3:5-*dibromo*-4-*aminobenzoate* has m. p. 127—128°; *ethyl* 2:4:6-*tribromobenzoate*, m. p. 80°. *Ethyl* 2:4:6-*tribromo*-3-*aminobenzoate*, m. p. 61—62°, was prepared from the silver salt of the acid and ethyl iodide. *Methyl* 2:4:6-*tribromo*-3-*aminobenzoate* has m. p. 96—97°. *Ethyl* 2:3:4:6-*tetrabromobenzoate* has m. p. 31°; iso*butyl* p-*nitrobenzoate* has m. p. 64—65°; *propyl* 3:5-*dinitrobenzoate* has m. p. 71°; iso*butyl* 3:5-*dinitrobenzoate* has m. p. 85°; *ethyl* 2:6-*dinitrobenzoate* has m. p. 75·5°.

W. G.

Preparation of *p*-Carbamidophenylacetylcarbamide and Related Compounds. MARY RISING (*J. Amer. Chem. Soc.*, 1920, **42**, 128—136. Compare Rising and Stieglitz, A., 1918, i, 271).—The successful preparation of *p*-carbamidophenylacetylcarbamide is described as the first of a series of carbamidophenylacylcarbamides which are intended to form a basis for the study of their physiological activity, particularly as hypnotics.

p-Nitrophenylacetyl chloride is condensed with carbamide in boiling benzene to yield *p*-nitrophenylacetylcarbamide, m. p. 237—239°, after preliminary softening and depending on the rate of heating (Jacobs and Heidelberger, A., 1918, i, 90, give m. p. 250—252°). This substance is quantitatively reduced by a solution of stannous chloride in cold glacial acetic acid which has been saturated with hydrogen chloride to p-*aminophenylacetylcarbamide*, which decomposes without melting at 192—193°, and, in the form of its *hydrochloride*, is converted by potassium cyanate into p-*carbamidophenylacetylcarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$.

The preparation of the following related carbamide derivatives is also described: methyl *p*-aminophenylacetate, b. p. 140—150°/17 mm., and its hydrochloride from *p*-aminophenylacetonitrile; p-*carbamidophenylacetonitrile*, m. p. 170·5°, from potassium cyanate and *p*-aminophenylacetonitrile hydrochloride; *methyl* p-*carbamidophenylacetate*, colourless, shining needles, m. p. 131—132°, by the esterification of *p*-carbamidophenylacetonitrile and from methyl *p*-aminophenylacetate hydrochloride and potassium cyanate; *p*-carbamidophenylacetic acid, m. p. 184—185° (decomp.), by hydrolysis of the corresponding methyl ester.

The ethylation of phenylacetonitrile with metallic sodium or sodamide and ethyl iodide is fully discussed. H. W.

α-Bromo-*o*- and -*p*-nitrocinnamic Acids. S. REICH and N. Y. CHANG (*Helv. Chim. Acta*, 1920, **3**, 235—240).—A mixture of the two stereoisomeric ethyl α-bromo-*p*-nitrocinnamates is produced in quantitative yield when an alcoholic solution of equimolecular proportions of ethyl αβ-dibromo-β-*p*-nitrophenylpropionate and anhydrous sodium acetate is boiled for two hours. The esters may be separated mechanically after crystallisation from light petroleum, and undergo hydrolysis to the respective acids by treatment at 100° with a mixture of glacial acetic acid (five parts), sulphuric acid (one part), and water (one part). *allo*-α-Bromo-*p*-nitrocinnamic acid, like its meta-isomeride (Reich and others, A., 1918, i, 262), does not undergo condensation into a dibromodinitrotruxone when treated with sulphuric acid; it is unchanged by the cold acid, whilst at 100° it is converted into its stable isomeride. *Ethyl* allo-*α-bromo-o-nitrocinnamate*,

$NO_2\cdot C_6H_4\cdot CH{:}CBr\cdot CO_2Et$,

is a yellow oil, which does not solidify, and results as the sole product of the action of sodium acetate on ethyl αβ-dibromo-β-*o*-nitrophenylpropionate. By hydrolysis under the above conditions, it is converted into the stable form of the corresponding acid (Naar, A., 1882, 840), the stability of the *allo*-forms of the three *allo*-α-bromonitrocinnamic acids and their esters increasing in the order ortho-, meta-, para-. αβ-Dibromo-β-*p*-nitrophenylpropionic acid furnishes a *bromo*-p-*nitrostyrene*, $NO_2\cdot C_6H_4\cdot CH{:}CHBr$, pale yellow needles, m. p. 45—46°, by treatment with sodium acetate in absolute alcoholic solution; if aqueous sodium acetate or sodium carbonate be used, a *stereoisomeride*, pale yellow needles, m. p. 123°, is obtained. The same tribromo-compound, m. p. 83°, is produced from each by the action of bromine. *Bromo-o-nitrostyrene*, $NO_2\cdot C_6H_4\cdot CH{:}CHBr$, is similarly obtained in two forms, yellow, m. p. 70°, and a yellow oil, which each furnish a tribromo-compound, m. p. 80°. J. K.

Influence of the Weight of Radicles on the Isomerisation of Ethylenic Compounds. S. REICH and RENÉE COUCHET (*Helv. Chim. Acta*, 1920, **3**, 240—243).—allo-*α-Bromocinnamtribromo*-

anilide, $C_{15}H_9ONBr_4$, m. p. 193°, accompanied by a small quantity of the *di*allo-*a-bromocinnamyl derivative*,

$$[CHPh:CBr\cdot CO]_2:N\cdot C_6H_2Br_3,$$

m. p. 150°, was prepared from the acid by treatment successively with phosphorus pentachloride in ethereal solution and tribromoaniline in benzene solution. By exposure in benzene solution to light for sixty hours, or in presence of bromine in chloroform solution, it is changed into the stable *isomeride*, needles, m. p. 150°. This compound was also prepared in a similar manner from its acid, the treatment with phosphorus pentachloride being carried out in boiling toluene solution. *allo*-a-Bromocinnamic anhydride (Michael and Bucher, A., 1898, i, 256) is produced by the action of acetic anhydride on the acid. It is isomerised by exposure to light for two weeks, but not by bromine. The latter result is possibly due to failure of the bromine to attach itself to the double bond rather than to the weight of the radicle. Stable *a-bromocinnamic anhydride*, $C_{18}H_{18}O_3Br_2$, prepared in a similar manner, forms needles, m. p. 100°. J. K.

The Truxillic Acids. A. W. K. de Jong (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 509—511).—The truxillic acids may best be separated from cinnamic acid by sublimation in a current of air at 130°. The truxillic acids may be separated from one another by the following process. The mixture of acids is dissolved in the calculated quantity of $N/10$-potassium hydroxide, and to the solution 1·5 grams of anhydrous calcium chloride are added for each 10 c.c. After twenty-four hours, the precipitated calcium salts of β-, δ-, and ε-truxillic acids are filtered off. The other acids are separated from the filtrate by hydrochloric acid and ether, and the process as above is repeated. To the final filtrate 8·5 grams of calcium chloride are added for each 10 c.c., the calcium salt of β-cocaic acid being precipitated and filtered off. From the filtrate, a- and γ-truxillic acids are separated by hydrochloric acid and ether, and the γ-acid is finally separated from the a-acid by its solubility in hot water. The mixture of calcium salts of β-, δ-, and ε-truxillic acids, obtained as above, is converted into the barium salts, which are separated by their varying solubility in water.

β-Cocaic acid gives with cinnamic acid a crystalline double acid, m. p. 139°. The ammonium salts of the truxillic acids slowly lose their ammonia when their aqueous solutions are evaporated on a water-bath, and are transformed into the free acids. W. G.

Action of Cyanogen Bromide on Hydrocarbons and Phenol Ethers under the Influence of Aluminium Chloride. P. Karrer, A. Rebmann, and E. Zeiler (*Helv. Chim. Acta*, 1920, **3**, 261—272).—A study of the range of applicability of the process for the synthesis of nitriles recently described (A., 1919, i, 591). Excellent yields were obtained of 3-cyanoacenaphthene and 2-cyanothiophen (owing to the agreement in properties between

the 2- and the 3-isomerides, the constitution given in the latter case is only presumed); less satisfactory results are obtained with *m*-methyl-*tert.*-butylbenzene, which gives a mixture, probably of 4- and 6-cyano-derivatives, and naphthalene, which also gives a mixture. Acenaphthylene, indene, and diphenyl were unchanged. The phenol ethers give even better results than the hydrocarbons; 2:4-dimethoxy-, 2:5-dimethoxy-, 3:4-dimethoxy-, and 2:3:4-trimethoxy-benzonitriles, 4-ethoxy- and 2-methoxy-naphthonitriles, were satisfactorily obtained from the corresponding ethers, being usually accompanied by small amounts of hydroxy-nitriles, due to hydrolysis of the alkyloxy-groups by aluminium chloride. Diphenyl and anthranol methyl ethers were recovered unchanged. Cyanogen chloride gives the same products as the bromide, and is almost equally reactive. Cyanogen iodide, however, is less useful, since it suffers decomposition to a considerable extent. The use of cyanogen bromide which has been kept for some time leads, in the case of benzene, to the formation of cyaphenin. As this was the sole product obtained by Scholl and Nörr in their original study of the reaction (A., 1900, i, 386), it would appear that they used polymerised material.

4-*Ethoxynaphthonitrile*, $OEt\cdot C_{10}H_6\cdot CN$, m. p. 85°, is hydrolysed by alcoholic potash to the corresponding acid; 2-*methoxynaphthonitrile*, $OMe\cdot C_{10}H_6\cdot CN$, m. p. 94°, however, only yields the 2-*methoxynaphthamide*, $OMe\cdot C_{10}H_6\cdot CO\cdot NH_2$, m. p. 150°. 2:3:4-*Trimethoxybenzonitrile*, $C_6H_2(OMe)_3\cdot CN$, fine needles, m. p. 58°, 1:3-dimethoxybenzonitrile, $C_6H_3(OMe)_2\cdot CN$, m. p. 89°, and 2-*hydroxy-4-methoxybenzonitrile*, $OH\cdot C_6H_3(OMe)\cdot CN$, m. p. 151°, furnish the corresponding acids. A *monomethyl ether* of 2:5-*dihydroxybenzonitrile*, $OH\cdot C_6H_3(OMe)\cdot CN$, has m. p. 122°.

J. K.

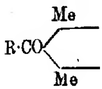
Synthesis of Monobasic Acids by the Action of Malonic Acid on the Substituted Benzhydrols. Replacement of the Hydroxyl by the Group $\cdot CH_2\cdot CO_2H$. R. Fosse (*Ann. Chim.*, 1920, [ix], **13**, 105—120).—A full account of work already published (compare A., 1907, i, 136). W. G.

The Constitution of the Dimethyl*cyclo*hexanone obtained by Methylation of the Sodium Derivative of α-Methyl*cyclo*hexanone. A. Haller and R. Cornubert (*Compt. rend.*, 1920, **170**, 700—705).—A further study of the dimethyl derivative obtained by the action of methyl iodide on α-methyl*cyclo*hexanone in the presence of sodamide (compare Haller, A., 1913, i, 984). Benzaldehyde condenses with this dimethyl*cyclo*hexanone in the presence of sodium ethoxide to give a benzylidene derivative, m. p. 82—82·5° (compare Auwers and Krollpfeiffer, A., 1915, i, 818). If the condensation occurs in the presence of dry hydrogen chloride, several products are obtained, of which the principal one is the benzylidene derivative mentioned above. In addition, the authors have isolated an isomeric *substance*, a yellow liquid, b. p. 197—198°/28 mm. (corr.), and two isomeric, crystal

line *compounds*, $C_{22}H_{24}O_2$, one having m. p. 117—118°, and the other m. p. 188—190°, which are apparently products of the abnormal condensation of one molecule of dimethyl*cyclo*hexanone with two molecules of benzaldehyde. The authors agree with Auwers and Krollpfeiffer (*loc. cit.*) that the dimethyl*cyclo*hexanone under examination is a 1 : 1-dimethyl-2-compound.

W. G.

Condensation of Acetophenone by means of Sodium Ethoxide. II. C. Castaldi (*Gazzetta*, 1920, **50**, i, 71—81. Compare A., 1916, i, 31).—The author has investigated further the compound, m. p. 182°, obtained as one of the products of the condensation of acetophenone with sodium ethoxide (*loc. cit.*). This compound is probably identical with the one, m. p. 183°, obtained by Stobbe (A., 1901, i, 549) by condensing acetophenone with ethyl malonate by means of dry sodium ethoxide in presence of anhydrous ether; this author attributed to it the formula $C_{24}H_{18}O$, and, on the basis of its failure to react with phenylhydrazine or hydroxylamine, considered that the oxygen atom is not present as carbonyl. By the work of Feith and Davies (A., 1892, 314), Hantzsch (A., 1891, 35), and Baum (A., 1896, i, 222), it has, however, been shown that the carboxylic oxygen of the group (annexed formula) reacts with phenylhydrazine or hydroxylamine only when R is a carboxyl group, and not when it is either methoxyl or phenyl.



Gentle oxidation of the compound with nitric acid yields either 6-benzoyl-3 : 5-diphenylbenzoic acid or 4-benzoyl-3 : 5-diphenylbenzoic acid, the sodium salt of which yields 1 : 3-diphenylbenzene, carbon dioxide, and benzene (?) when dry-distilled. The compound must, therefore, be regarded as either 6-benzoyl-3 : 5-diphenyltoluene or 4-benzoyl-3 : 5-diphenyltoluene, and confirmation of this structure is afforded by the fact that it is obtainable also by the action of benzoyl chloride on 3 : 5-diphenyltoluene in carbon disulphide solution and in presence of aluminium chloride.

6-*Benzoyl*-3 : 5-*diphenyltoluene* or 4-*benzoyl*-3 : 5-*diphenyltoluene*, $C_{26}H_{20}O$, forms shining laminæ, m. p. 186° (not 182° as previously stated), has the normal molecular weight in freezing benzene, and dissolves in cold concentrated sulphuric acid, giving an intense violet-red solution.

6-*Benzoyl*-3 : 5-*diphenylbenzoic acid* or 4-*benzoyl*-3 : 5-*diphenylbenzoic acid*, $C_{26}H_{18}O_3$, forms faintly yellow, prismatic needles, m. p. 240° (decomp.), and dissolves in the cold in concentrated sulphuric acid, giving an intense violet coloration. The *sodium* salt ($+ 4H_2O$) was prepared.

Diphenylbenzyltoluene, $C_6H_2MePh_2 \cdot CH_2Ph$, obtained by reducing the benzoyldiphenyltoluene by means of red phosphorus and hydriodic acid, crystallises in colourless needles, m. p. 125°, and gives no coloration with concentrated sulphuric acid.

T. H. P.

Reduction and Fission of Halogenated Ketones by Tertiary Bases. KARL VON AUWERS and ELISABETH LÄMMERHIRT (*Ber.*, 1920, **53**, [*B*], 428—443).—The conversion of *m*-α-bromo*iso*butyryl-*p*-cresol into 3:6-dimethylchromanone by the action of boiling dimethyl- or diethyl-aniline (A., 1914, i, 1136) does not appear to be an instance of a general reaction, since the examination of a series of α-halogenated acyl-*p*-cresols shows that, as a rule, the parent halogen-free compound is regenerated, whilst chromanones or coumaranones are only formed in relatively small amount. The detection of coumaranones in the presence of keto-phenols is best effected with the aid of *p*-nitrophenylhydrazine, which converts the former into the sparingly soluble dinitro-osazones of the corresponding diketones, and the latter into the more readily soluble nitrophenylhydrazones. The same reagent may be used to distinguish between coumaranones and chromanones, since the latter, like the monocyclic ketones, only yield readily soluble mono-derivatives. The separation of keto-phenols and chromanones is not smoothly effected by treatment with alkali hydroxides, and is best accomplished by protracted warming of the mixture with semicarbazide. Mixtures of free keto-phenols and their ethers, such as are frequently obtained by the condensation of phenol ethers with acid chlorides in the Friedel-Craft's reaction, are not readily separated by means of alkali hydroxide and ether; removal of the phenols is, however, effected by shaking the solution of the mixed substances in light petroleum with aqueous methyl-alcoholic potassium hydroxide solution (compare Claisen, A., 1919, i, 266).

o-Chloroacetyl-*p*-cresol, when boiled with diethylaniline, is mainly converted into 4-methylcoumaranone (identified as the *dinitro-osazone* of p-*tolylglyoxal*, m. p. 260—265° [subsequent communication]), small amounts of acetyl-*p*-cresol (p-*nitrophenylhydrazone*, orange-red, shining needles, m. p. 245—246°) being also formed. Under similar conditions, *o*-α-chloropropionyl-*p*-cresol gives *o*-propionyl-*p*-cresol (p-*nitrophenylhydrazone*, m. p. 185—186°) and a little 1:4-dimethylcoumaranone. *o*-α-Bromo-*n*-butyryl-*p*-cresol yields *o*-*butyryl*-p-*cresol*, coarse, shining prisms, m. p. 33—34° (*semicarbazone*, long needles, m. p. 188—189°), and 2:6-dimethylchromanone. *o*-α-Chloro*iso*valeryl-*p*-cresol is smoothly reduced by dimethyl- or diethyl-aniline to o-*isovaleryl*-p-*cresol* (p-*nitrophenylhydrazone*, orange-red, silky needles, m. p. 136—137°; *semicarbazone*, coarse needles or prisms, m. p. 203—204°, when rapidly heated). The identity of the ketone is established by its synthesis from *iso*valeryl chloride and *p*-tolyl methyl ether; it has b. p. 151°/21 mm., $D_4^{18\cdot4}$ 1·0291, D_4^{20} 1·028, $n_\alpha^{18\cdot4}$ 1·52683, $n_D^{18\cdot4}$ 1·53270, $n_\beta^{18\cdot4}$ 1·55001, $n_\gamma^{18\cdot4}$ 1·56848, n_D^{20} 1·5320. α-*Bromo*-n-*butyrophenone*, colourless, mobile oil, b. p. 145—147°/14 mm., $D_4^{13\cdot25}$ 1·3724, D_4^{20} 1·364, $n_\alpha^{13\cdot25}$ 1·55996, $n_D^{13\cdot25}$ 1·56520, $n_\beta^{13\cdot25}$ 1·58035, $n_\gamma^{13\cdot25}$ 1·59378, n_D^{20} 1·5622, is prepared from α-bromo-*n*-butyryl bromide, benzene, and aluminium chloride, and is converted by diethylaniline into *butyrophenone*, pale yellow oil, b. p. 120—125°/21 mm. (p-*nitrophenylhydrazone*, orange-red needles,

m. p. 161·5—162·5°). *α-Bromo*iso*butyrophenone* is a pale yellow oil, b. p. 135—137°/17 mm., $D_4^{14.4}$ 1·3613, D_4^{20} 1·355, $n_\alpha^{14.4}$ 1·55425, $n_D^{14.4}$ 1·55923, $n_\beta^{14.4}$ 1·57369, $n_\gamma^{14.4}$ 1·58617, n_D^{20} 1·5567, which is transformed by diethylaniline into a mixture of approximately equal quantities of *iso*propyl- and *iso*propenyl-phenyl ketones. α-Bromo*iso*butyryl bromide reacts with *m*-5-xylenol methyl ether in the presence of aluminium chloride to yield 1:1:3:5-*tetramethylcoumaranone* and 2-iso*butyryl*-m-5-*xylenol*, m. p. 93—94°, the partial reduction of the brominated ketone primarily formed being effected by the liberated hydrogen bromide.

The conversion of α-bromo*iso*butyryl-*p*-cresol into *p*-cresotic acid by boiling pyridine has been previously described (Auwers, *loc. cit.*); the same acid is similarly obtained from the α-chloro-derivatives of *o*-propionyl-, *o*-butyryl-, and *o*-*iso*valeryl-*p*-cresol. Hydroxyl-free, halogenated ketones behave in the same manner; thus, benzoic acid is obtained from α-bromo-*n*-butyro- and α-bromo*iso*butyro-phenones. It appears possible that the first step in the action consists in the withdrawal of halogen acid from the compound, with the formation of a substance with an unsaturated side-chain; *p*-tolyl *iso*butenyl ketone is, however, unaffected by protracted boiling with pyridine. The action of quinoline differs from that of pyridine, since, for example, cresotic acid is not produced when it reacts with α-chloro*iso*valeryl-*p*-cresol; small quantities of 2:2:6-trimethylchromanone can, however, be isolated.

H. W.

The Reduction of Aromatic Ketones. W. D. Cohen (*Rec. trav. chim.*, 1920, **39**, 243—279).—It has previously been shown (A., 1919, i, 124, 210) that in acid solution, benzophenone is reduced, with the formation of benzopinacone, whilst in alkaline medium, benzhydrol is the product. When the reducing agent is aluminium amalgam, a mixture of the two is obtained, the amount of benzhydrol depending on the rate at which the pinacone is attacked, owing to the slightly alkaline reaction set up at the moment of reduction. It is now shown that in an absolutely neutral medium, the benzophenone being reduced in absolute alcohol by means of light, benzopinacone is the only product. The velocity of formation of benzopinacone under these conditions is proportional to the concentration of the alcohol and the amount of active light, but is independent of the concentration of the ketone. The thermal coefficient of this photochemical reaction is small, being about 1·1 for 10°. The velocity of the reaction depends to some extent on the character of the alcohol, but the nature of the ketone is the principal factor in directing the reaction. Substituted ketones are attacked less quickly than benzophenone itself. The relationships observed between the different ketones are independent of the alcohol used. This photochemical reduction of aromatic ketones by alcohols in sunlight is an irreversible reaction.

The actinic light is situated in the violet part of the visible spectrum, and probably in the neighbourhood of the rays 404·7 and 407·8 $\mu\mu$. The absorption of the ketones is selective. In a mixture of two ketones, one of them may absorb a part of the light necessary for the reduction of the other, and there may thus be a disturbance in the relative rates of reduction. W. G.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. V. *p*-Hydroxybenzophenones. P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 339—349. Compare A., 1917, i, 143). —4-Hydroxybenzophenone does not undergo any reduction when boiled with alcoholic potassium hydroxide even for six days, and the introduction of a chlorine or bromine atom into the para-position in the other nucleus has no influence.

4-Ethoxybenzophenone is slowly converted, under the same conditions, into 4-ethoxybenzhydrol, and the action is accelerated by the introduction of a chlorine or bromine atom into the *para*-position in the other nucleus. In this case, at the same time, a secondary reaction occurs, the chlorine or bromine becoming replaced by an ethoxy-group, giving 4:4′-diethoxybenzophenone.

The following new compounds are described: *4-chloro-4′-ethoxybenzophenone*, m. p. 121·25° (corr.), b. p. 223°/12 mm.; *4-chloro-4′-ethoxybenzhydrol*, m. p. 69·5° (corr.); *4:4′-diethoxybenzophenone*, m. p. 131·5° (corr.), b. p. 248°/15 mm.; *4-bromo-4′-ethoxybenzhydrol*, m. p. 80·5°. W. G.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. VI. Iodobenzophenones. P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 350—357. Compare preceding abstract).—Both 2-iodo- and 4-iodo-benzophenone are completely transformed into benzhydrol, the iodine being removed, when boiled with alcoholic potassium hydroxide. Under the same conditions, 3-iodobenzophenone is only partly converted into benzhydrol, part of it remaining unchanged. If an ethoxy-group is introduced into the iodobenzophenone, as in 4-iodo-4′-ethoxybenzophenone, the iodine is removed by boiling with alcoholic potassium hydroxide, but in this case the ethoxy-group exerts its influence in preventing the reduction, and the product is ethoxybenzophenone.

Chloro- and bromo-benzhydrols do not lose their halogen when boiled with alcoholic potassium hydroxide, but under similar conditions 4-iodobenzhydrol and, to a lesser extent, 3-iodobenzhydrol have their iodine removed.

m-Iodobenzoyl chloride condenses with benzene in sunlight in the presence of aluminium chloride to give *3-iodobenzophenone*, m. p. 42·5°, b. p. 226°/18 mm. It yields *3-iodobenzhydrol*, m. p. 54°. *4-Iodo-4′-ethoxybenzophenone*, m. p. 147·5°, b. p. 266°/17 mm., prepared from *p*-iodobenzoyl chloride and phenetole, gives *4-iodobenzhydrol*, m. p. 73°. W. G.

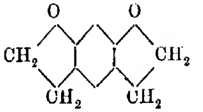
The Resin from Species of Xanthorrhœa not previously examined. EDWARD HENRY RENNIE, WILLIAM TERNENT COOKE, and HEDLEY HERBERT FINLAYSON (T., 1920, **117**, 338—350).

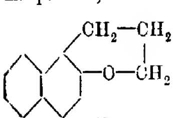
Glucosides. V. Synthesis of β-Gaultherin, of Methyl β-Tetra-acetylglucosidoanthranilate, and of β-Glucosidoresorcylic Acid Methyl Ether. P. KARRER and H. WEIDMANN (*Helv. Chim. Acta*, 1920, **3**, 252—257. Compare A., 1919, i, 594).—The action of diazomethane on an ice-cold alcoholic solution of glucosidosalicylic acid results in the formation of the *methyl* ester, $C_{14}H_{18}O_8$, associated with 1 mol. of alcohol of crystallisation, as leaflets, m. p. 90—92°, $[\alpha]_D^{15}$ −53·78° in alcohol. It is freed from alcohol by heating in a vacuum at 70°, and then has m. p. 105°. It gives no colour with ferric chloride and, whilst structurally identical with natural gaultherin, differs from it in that it is hydrolysed by emulsin, but not by gaultherase. Gaultherin is therefore the α-stereoisomeride. The *tetra-acetyl* derivative of the above ester, $C_{22}H_{26}O_{12}$, needles, m. p. 154°, $[\alpha]_D^{13}$ −44·77° in chloroform, is identical with Mauthner's product (A., 1918, i, 544), which therefore is not tetra-acetyl gaultherin. *Methyl β-tetra-acetylglucosidoanthranilate*, $C_{22}H_{27}O_{11}N$, prepared from the acid by treatment with diazomethane, forms needles, m. p. 165°, $[\alpha]_D$ −54·88° in chloroform. *β-Tetra-acetyl glucosido-4-methoxysalicylic acid*, $C_{22}H_{26}O_{13}$, m. p. 160°, $[\alpha]_D^{15}$ −48·81° in alcohol, is obtained by condensation of silver 4-methoxysalicylate with acetobromoglucose. It gives no colour with ferric chloride. By hydrolysis with cold baryta it yields *β-d-glucosido-4-methoxysalicylic acid*, needles, m. p. 163°, $[\alpha]_D^1$ −81·55° in water. It is hydrolysed by emulsin, and gives no colour with ferric chloride. The *tetra-acetylglucose* ester of 4-*methoxysalicylic acid*, $C_{22}H_{26}O_{13}$, is also produced in the above condensation. It forms needles, m. p. 147°, $[\alpha]_D^{16}$ −45·37° in chloroform. J. K.

Syntheses of Chromans [Benzopyrans] and Coumarans. II. R. E. RINDFUSZ, P. M. GINNINGS, and V. L. HARNACK (*J. Amer. Chem. Soc.*, 1920, **42**, 157—165).—The methods described previously (A., 1919, i, 342) have been applied to substituted phenols. In general, it is found that the dehydration of hydroxyethyl and hydroxypropyl phenyl ethers can be effected more conveniently with phosphoric oxide than with zinc chloride. The procedure consists in boiling the mixture of reagents for about an hour in the presence of an inert solvent (such as toluene or methyl ethyl ketone), the boiling point of which is such as to allow a fairly high temperature being attained without, however, rendering the subsequent fractionation of the product a matter of difficulty.

The following compounds are described: *o-tolyl γ-hydroxypropyl ether*, b. p. 174—176°/42 mm., D^{29} 1·053, n_D^{27} 1·523; *o-tolyl γ-bromopropyl ether*, b. p. 154—156°/20 mm., D^{29} 1·299, n_D^{27} 1·535; *8-methylbenzopyran*, b. p. 114—116°/20 mm., D^{29} 1·039, n_D^{27} 1·542; *o-tolyl β-hydroxyethyl ether*, b. p. 143—145°/20 mm., D^{29} 1·079, n_D^{27} 1·528;

o-tolyl β-bromoethyl ether, b. p. 133—134°/20 mm., D^{29} 1·360, n_D^{29} 1·544; *6-methylcoumaran*, b. p. 119—120°/65 mm., D^{29} 1·0·0, n_D^{29} 1·527; *p-bromophenyl γ-hydroxypropyl ether*, b. p. 206°/48 mm., D^{24} 1·442, n_D^{24} 1·563; *6-bromobenzopyran*, b. p. 143—144°/18 mm., D^{25} 1·465, n_D^{25} 1·580; *p-bromophenyl β-bromoethyl ether*, b. p. 165°/16 mm., m. p. 56°; *4-bromocoumaran*, b. p. 135°/20 mm., D^{20} 1·436, n_D^{20} 1·555; *p-bromophenyl β-hydroxyethyl ether*, b. p. 184°/20 mm., m. p. 49—50°; *m-phenylene di-β-hydroxyethyl ether*, $C_6H_4(O{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$, b. p. 230—234°/30 mm., m. p. 81°; *s-benzotetrahydrodifuran* (formula I), b. p. 110—113°/148 mm., D^{25} 0·861, n_D^{25} 1·448; *m-phenylene di-γ-hydroxypropyl ether*, b. p. 246—248°/20 mm., D^{31} 1·145, n_D^{31} 1·529; *s-benzotetrahydrodipyran*, b. p. 97°/75 mm., n_D^{31} 1·448; *β-naphthyl γ-hydroxypropyl ether*, m. p. 99—99·5°; *β-naphthadihydropyran* (formula II), m. p. 41—42°; *β-naphthyl β-hydroxyethyl ether*, m. p. 76—77°; *β-naphthadihydrofuran*, b. p. 185°/10 mm. (some decomp.), D^{30} 1·0066, n_D^{30} 1·482; *β-naphthyl β-bromoethyl ether*, m. p. 91·5—92·5°. H. W.


(I.)


(II.)

Synthesis of Acids by the Action of Acid Anhydrides on Alcohols containing a Pyran Ring. Replacement of the Hydroxyl by the Group $\cdot CH_2 \cdot CO_2H$ or the Group $\cdot CHR \cdot CO_2H$. R. FOSSE (*Ann. Chim.*, 1920, [ix], **13**, 87—104).—A full account of work already published (compare A., 1906, i, 691). W. G.

Constitution of Ephedrine. Deoxyephedrine. A. OGATA (*J. Pharm. Soc. Japan*, 1919, **451**, 751—764).—By a comparison of the physical constants of the two bases and of their salts, the author shows that deoxyephedrine is identical with *d*-β-phenyl*iso*propylmethylamine, prepared by reducing with sodium and alcohol the condensation product obtained by keeping a mixture of benzyl methyl ketone and alcoholic methylamine for four weeks, and resolving the racemic base obtained with tartaric acid. Consequently, ephedrine has the constitution OH·CHPh·CHMe·NHMe. CHEMICAL ABSTRACTS.

Metallic Salts of Pyrrole, Indole, and Carbazole. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1920, **24**, 81—99).—The "ammono-acids" (compare A., 1905, i, 582; 1912, ii, 437), pyrrole, indole, and carbazole, have been converted into their metallic salts by the action of metals (sodium, potassium, magnesium, or calcium) or the metal amides (sodium, potassium, silver) on solution of the "ammono-acids" in liquid ammonia. In the case of pyrrole, a crystalline potassium salt could not be obtained, and on evaporating the solution an amorphous, viscous mass was always produced. Sodium forms a crystalline compound with pyrrole, C_4H_4NNa,NH_3, on cooling the solution to the temperature produced by solid carbon dioxide and ether. This compound loses ammonia at 20° and yields the compound, C_4H_4NNa; it is hydrolysed by water, yielding pyrrole

and sodium hydroxide. *Calcium pyrrole*, $(C_4H_4N)_2Ca,4NH_3$, forms colourless crystals, but on losing its ammonia to form the "anammonous" salt it becomes slightly yellow, and has the dull appearance of an effloresced salt. It is vigorously attacked by water and pyrrole and calcium hydroxide are formed. In the preparation from metallic calcium it is shown that there is a deficiency in the hydrogen evolved which is due to the formation of a small amount of tetrahydropyrrole. *Magnesium pyrrole*, $(C_4H_4N)_2Mg,2NH_3$, forms colourless crystals. *Silver pyrrole*, C_4H_4NAg,NH_3, is a well-crystallised product, which on keeping rapidly turns grey, and finally becomes black. The sodium and potassium salts of indole both form amorphous, viscous masses, from which it was not possible to obtain crystals. *Calcium indole*, $(C_8H_6N)_2Ca,4NH_3$, forms beautiful, white crystals, which on heating to 100° decompose into indole and calcium amide. In the preparation about one-half of the indole was reduced to dihydroindole. *Magnesium indole*,

$$(C_8H_6N)_2Mg,4NH_3,$$

forms needle-shaped, colourless crystals which, although quite soluble in liquid ammonia when freshly prepared, after a time are not completely soluble. This is probably due to a decomposition with the formation of an insoluble product. *Silver indole*, C_8H_6NAg,NH_3, is an extremely soluble, crystalline compound which exhibits the phenomenon of supersaturation to a marked degree. *Potassium carbazoles*, $C_{12}H_8NK,2NH_3$ and $C_{12}H_8NK,NH_3$, form very soluble crystals, which lose their ammonia at 20°. *Silver carbazole*, $C_{12}H_8NAg,2NH_3$, is formed at −39°, and on warming loses one molecule of ammonia to give $C_{12}H_8NAg,NH_3$. *Calcium carbazole*, $(C_{12}H_8N)_2Ca,7NH_3$, forms yellow crystals with a green fluorescence at −39°, and on heating at 30° loses three molecules of ammonia to give $(C_{12}H_8N)_2Ca,4NH_3$. J. F. S.

Pyrrole-blacks. A. ANGELI and CORRADO LUTRI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 14—22. Compare A., 1919, i, 134).—In presence of water, pyrrole and *p*-benzoquinone rapidly react, giving first a reddish-brown, colloidal solution clearly showing Tyndall's phenomenon and then a black, amorphous powder closely resembling pyrrole-blacks and melanins; the mother liquor contains considerable proportions of quinol. The reaction takes place also in alcoholic, ethereal, or, more slowly, moist benzene solution. If the product of the reaction is washed with water and extracted with alcohol in a reflux apparatus, a black substance is obtained which, when heated, does not melt, but emits vapour which colours red a pine splinter moistened with hydrochloric acid; it dissolves in alkali hydroxide solution, giving an intense brownish-black coloration, but is insoluble in alkali carbonate solution. The percentage compositions of two preparations are: C, 69·14—69·22 (68·75—68·85); H, 2·86—2·90 (2·80—2·84); N, 6·11 (—), and the compound is probably formed by the interaction of 3 mols. and 5 mols., or 4 mols. and 7 mols., of pyrrole and *p*-benzoquinone respectively. The conclusion is drawn that the melanins represent complex molecules

similar to the polysaccharides, polypeptides, polyterpenes, caoutchouc, etc., the tendency to polymerise being due partly to the presence of conjugated double linkings in the pyrrole molecule. Under the same conditions indole does not react with pyrrole.

Similarly, pyrrole and 1:4-naphthaquinone interact, yielding naphthaquinol and a *compound*, $C_{34}H_{19}O_5N$ (?), which crystallises in violet-black needles and, when heated, melts incipiently and at the same time emits vapour giving a red coloration to a pine splinter moistened with hydrochloric acid; it is readily decomposed by hot potassium hydroxide solution with formation of an orange-coloured product very sparingly soluble in the ordinary solvents. The compound appears to be formed by the condensation of 1 mol. of pyrrole with 3 mols. of the naphthaquinone.

Isatin and pyrrole also react readily (compare Liebermann and Kraus, A., 1907, i, 657).

Oxidation of pyrrole by means of hydrogen peroxide yields (1) a pyrrole-black, and (2) a *compound*, $C_8H_{10}ON_2$, which crystallises in shining, almost colourless needles, m. p. 136°, and at about 200° in presence of air blackens and emits vapour giving an intense red coloration to a pine splinter moistened with hydrochloric acid. By a few drops of dilute sulphuric acid and a trace of dichromate this compound is coloured brown, a black powder being slowly deposited. With nitrous acid or ferric chloride it gives a yellow coloration and, later, a black powder. With a trace of nitroprusside and potassium hydroxide it yields a brilliant violet coloration turned deep blue by acetic acid.

T. H. P.

Benzidino-quinones and Bisquinonylbenzidines as Vat Dyes. Kurt Brass and Otto Papp (*Ber.*, 1920, **53**, [*B*], 446—462). —Previous attempts to study the primary product of the interaction of benzidine on *p*-benzoquinone (Brass, A., 1913, i, 1232) were rendered difficult on account of the readiness with which it loses a molecule of benzidine to yield quinonebenzidine, which is subsequently readily polymerised. More successful attempts are now described in which substituted quinones are employed.

Benzidino-toluquinone is prepared by the action of a solution of benzidine in 50% acetic acid on a hot aqueous solution of toluquinone; it forms a dark violet powder, which is decomposed by prolonged contact with air. By reduction with hyposulphite in very faintly alkaline solution, it yields a yellow vat, from which cotton is dyed in brown shades, which, however, are due to the polymerised form of the dye. The free amino-group shows little tendency to enter into action, but its presence is established by the isolation of N-p-*chlorobenzylidenebenzidino-toluquinone*,

$$C_6H_2O_2Me\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4Cl.$$

Methylanilino-*p*-benzoquinone condenses with benzidine in alcoholic solution to yield a mixture of 2-benzidino-5-methylanilinobenzoquinone, m. p. 216—217° (corr.) [H. and W. Suida, A., 1919, i, 81, give 215—218°], and relatively small amounts of NN′-*bis-5-methylanilinobenzoquinonyl-2-benzidine*, $[NMePh\cdot C_6H_2O_2\cdot NH\cdot C_6H_4-]_2$,

m. p. 254° (decomp.). The substances have similar tinctorial properties, and dye cotton in yellowish-brown shades from a yellow vat. 2-*Di-o-anisidino-5-methylanilinobenzoquinone*,

$$NMePh\cdot C_6H_2O_2\cdot NH\cdot C_6H_3(OMe)\cdot C_6H_3(OMe)\cdot NH_2,$$

brown leaflets, m. p. 124—128° (decomp.) after softening from 120°, and NN′-*bis-5-methylanilinobenzoquinonyl-2-dianisidine*, $[NMePh\cdot C_6H_2O_2\cdot NH\cdot C_6H_3(OMe)-]_2$, brown needles, m. p. 244—246° (corr.), are prepared from methylanilinobenzoquinone and di-*o*-anisidine, and are separated by taking advantage of the greater solubility of the latter in acetone; on cotton, they yield brown shades with a tendency towards olive.

Another ready method of preparing simple vat dyes consists in the oxidation of anilino-quinones to benzidine derivatives (compare Brass, A., 1912, i, 874); 2-anilino-3:5:6-trichlorobenzoquinone, however, is converted by manganese dioxide in the presence of sulphuric acid into 3′-*anilino-2′:5′:3:5:6-pentachlorodibenzoquinonylaniline*, $C_6O_2Cl_3\cdot NPh\cdot C_6O_2Cl_2\cdot NHPh$, microcrystalline, bluish-grey leaflets, which does not melt below 300° and dyes cotton in dull brown shades.

Whilst benzidine and α-naphthaquinone yield only 2-benzidino-α-naphthaquinone (Pummerer and Brass, A., 1911, i, 655), it is found that dianisidine, under similar conditions, gives NN′-*bis-α-naphthaquinonyl-2-dianisidine*, $[C_{10}H_5O_2\cdot NH\cdot C_6H_3(OMe)-]_2$, brownish-violet, crystalline powder, m. p. 303—305°, which dyes cotton in violet shades. In a similar manner, NN′-*bis-3-chloro-α-naphthaquinonyl-2-dianisidine*, red needles, m. p. 270—272°, is prepared from 2:3-dichloro-α-naphthaquinone; it gives brownish-violet shades on cotton. *o*-Ethoxybenzidine and α-naphthaquinone yield NN′-*bis-α-naphthaquinonyl-3-ethoxybenzidine*,

$$C_{10}H_5O_2\cdot NH\cdot C_6H_3(OEt)\cdot C_6H_4\cdot NH\cdot C_{10}H_5O_2,$$

slender, violet-brown needles, m. p. 279—281°, which dyes cotton in violet shades. H. W.

Four-membered Cyclic Ureas. III. Condensation of *iso*Cyanic Acid with Alkyl Schiff Bases and Related Compounds. WILLIAM J. HALE and NORBERT A. LANGE (*J. Amer. Chem. Soc.*, 1920, **42**, 107—116).—Further investigation shows that the condensation of *iso*cyanic acid with Schiff bases which contain an alkyl group attached to the nitrogen atom proceeds in the same manner as with benzylidene-ethylamine (A., 1919, i, 225). The reaction has been further extended to substances which contain the carbimino-nucleus attached to a nitrogen atom, and, in the special instance of benzylbenzylidenehydrazone,

$$CHPh{:}N\cdot NH\cdot CH_2Ph,$$

the results obtained confirm those of Bailey and Moore (A., 1917, i, 355).

4:6-*Diketo-2-phenyl-1-propylhexahydro-1:3:5-triazine*,

$$CHPh\Big\langle{NPr\cdot CO \atop NH-CO}\Big\rangle NH,$$

colourless, flaky needles, m. p. 211°, is prepared by the gradual

addition of powdered potassium cyanate to a well-cooled solution of benzylidene-*n*-propylamine in glacial acetic acid; the corresponding *monoacetyl* derivative forms colourless prisms, m. p. 120°. 4:6-*Diketo-2-phenyl-1-butylhexahydro-1:3:5-triazine* is prepared in a similar manner and has m. p. 188°, whilst 4:6-*diketo-2-phenyl-1-amylhexahydro-1:3:5-triazine* has m. p. 202°.

Benzylbenzylidenesemicarbazone (Bailey and Moore, *loc. cit.*) is slowly hydrolysed when treated with steam in the presence of hydrochloric acid to benzaldehyde and benzylhydrazine hydrochloride, the action proceeding as indicated by the scheme:

$$CH_2Ph\cdot N(CO\cdot NH_2)\cdot N{:}CHPh \longrightarrow CH_2Ph\cdot N(CO\cdot NH_2)\cdot NH_2 \longrightarrow CH_2Ph\cdot NH\cdot NH_2.$$

A mixture of 2-benzylsemicarbazide, $CH_2Ph\cdot N(CO\cdot NH_2)\cdot NH_2$, m. p. 135—136°, and 1-benzylsemicarbazide,

$$CH_2Ph\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 155°, is obtained by the cautious addition of potassium cyanate to a concentrated, ice-cold, aqueous solution of benzylhydrazine hydrochloride; the two substances are readily separated by taking advantage of the sparing solubility of the latter in cold chloroform, in which the former is freely soluble (compare Curtius, A., 1910, i, 610; Busch, Opfermann, and Walther, A., 1904, i, 628; Kessler and Rupe, A., 1912, i, 219). The 2-derivative is smoothly transformed into the 1-compound when heated for a few minutes at its melting point.

as-Diphenylbenzylidenehydrazine, $CHPh{:}N\cdot NPh_2$, phenylbenzylidenehydrazine, and 2-benzyl-1-benzylidenesemicarbazone could not be caused to condense with *iso*cyanic acid. H. W.

Origin of the Humin formed by the Acid Hydrolysis of Proteins. IV. Hydrolysis in the Presence of Aldehydes. III. Comparative Hydrolysis of Fibrin and Gelatin in the Presence of Various Aldehydes. George E. Holm and Ross Aiken Gortner (*J. Amer. Chem. Soc.*, 1920, **42**, 632—640).—Previous work on the influence of the presence of aldehydes on the nature of the products obtained by acid hydrolysis of proteins (A., 1918, i, 84) has been extended by the hydrolysis of fibrin and gelatin in presence of benzaldehyde, acetaldehyde, butaldehyde, and *iso*butaldehyde. Whilst the proportions of "ammonia" and soluble humin nitrogen are not appreciably altered, that of acid-insoluble humin nitrogen increases rapidly to a maximum with increase in the quantity of benzaldehyde used. This result is ascribed to the presence of both tryptophan and tyrosine. Butaldehyde and *iso*butaldehyde are similar in their effects to benzaldehyde, but they give rise to black, insoluble residues, possibly the result of their polymerisation. This change is much more marked in the case of acetaldehyde, and consistent results are therefore not obtained. Whilst the total amino-nitrogen in the filtrate from the soluble humin diminishes rapidly when hydrolysis is carried out in presence of increasing amounts of formaldehyde, probably owing to condensation of formaldehyde with amino-acids, only a slight decrease is

observed when benzaldehyde, or butaldehyde, or *iso*butaldehyde is used. J. K.

Distribution of Basic Nitrogen in Phaseolin. A. J. FINKS and CARL O. JOHNS (*J. Biol. Chem.*, 1920, **41**, 375—377).—The average values are: cystine, 0·84%; arginine, 6·11%; histidine, 3·32%, and lysine, 7·88%. The latter value is considerably higher than that obtained by the direct method of Kossel and Patten (A., 1903, ii, 582). J. C. D.

Effect of Poisons on an Enzymatic Process. V. Alkaloids, Caffeine. C. G. SANTESSON (*Skand. Arch. Physiol.*, 1919, **39**, 132–166; from *Chem. Zentr.*, 1920, i, 392. Compare A., 1915, i, 728).—In continuation of previous investigations, the influence of the following substances on the power of the catalase of frog's muscle to effect the decomposition of hydrogen peroxide has been studied: pyridine, quinoline, quinine, quinine hydrochloride and hydrobromide, veratrine, veratrine hydrochloride, caffeine, nicotine and its hydrochloride, veratrine (Swedish pharmacopœia), coniine and its hydrochloride, morphine and its hydrochloride, dionine, diacetylmorphine (base and hydrochloride), cocaine (base and hydrochloride), atropine (base and sulphate), strychnine, and aconitine (base and acid hydrochloride). The majority of the free alkaloids, even in very dilute solution, facilitate the action of the catalase to a marked degree, and a similar effect is observed with pyridine; little or no activation is observed only with quinoline, coniine, and caffeine. The alkaloidal salts, on the other hand, generally have a restraining action; nicotine hydrochloride, ethylmorphine (dionine), and atropine sulphate are exceptions in this respect. H. W.

Composition of Salvarsan. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1920, **117**, 370—377).

Silver Salvarsan. A. BINZ, H. BAUER, and A. HALLSTEIN (*Ber.*, 1920, **53**, [*B*], 416—428).—From a study of silver salvarsan and allied substances, the authors are led to the following conclusions: (1) colloidal silver is not present in silver salvarsan; (2) two molecules of silver nitrate react with one molecule of salvarsan or its derivative; (3) silver salvarsan contains silver oxide in complex form; (4) Karrer's hypothesis that the silver atoms are united by the residual affinities of the arsenic atoms is not established, since this would indicate a tendency for the latter to pass into the quinquevalent state, whereby they would lose therapeutic power; probably the amino-groups, the capacity of which to take part in complex salt formation is well established, are responsible for the formation of metallic derivatives, or, as recently suggested by Dilthey, the metallic atoms may be united to the molecule as a whole, and not to any particular group.

3-Amino-4-hydroxyphenylarsinic acid is diazotised and converted into 3-chloro-4-hydroxyphenylarsinic acid, which, on nitration, yields 3-chloro-5-nitro-4-hydroxyphenylarsinic acid; the latter is

reduced by hyposulphite to 5:5′-dichloro-3:3′-diamino-4:4′-dihydroxyarsenobenzene, the *dihydrochloride* of which,

$$C_{12}H_{10}O_2N_2Cl_2As_2,2HCl,2MeOH,$$

forms greenish-yellow flocks, and is transformed by silver nitrate into *dichlorosalvarsan di-silver chloride*,

$$As_2[C_6H_2Cl(OH)\cdot NH_2]_2,2AgCl,$$

yellow, gelatinous precipitate. The corresponding copper salt, $As_2[C_6H_2Cl(NH_2)\cdot O\,cu]_2CuCl_2$, is yellowish-brown.

3 : 3′-*Diamino*-4 : 4′-*dihydroxyarsenobenzene di-silver iodide*, $As_2[C_6H_3(NH_2)\cdot OH]_2,2AgI$, is prepared by successive treatment of an aqueous solution of the salvarsan base with hydriodic acid and silver nitrate, and forms an orange-coloured colloidal precipitate. Attempts to convert it into the silver salvarsan base,

$$As_2[C_6H_3(NH_2)\cdot OH]_2,Ag_2O,$$

by means of sodium carbonate were not completely successful, since oxidation occurred during the washing of the primary black precipitate. When treated with sodium hydroxide, it gives the soluble sodium salt of silver salvarsan, in which the absence of colloidal silver or silver oxide is demonstrated by ultra-filtration experiments, by the absence of the Tyndall phenomenon, and by the appearance under the ultramicroscope. When copper chloride and salvarsan are mixed in aqueous solution, a yellow precipitate of 3:3′-*diamino*-4:4′-*dihydroxyarsenobenzene mono-copper chloride hydrochloride*, $As_2[C_6H_3(OH)\cdot NH_2]_2,CuCl_2,HCl$, is obtained.

3:5:3′:5′-Tetrabromo-*p*-arsenophenol is mainly oxidised by silver nitrate in pyridine methyl-alcoholic solution, yielding, amongst other products, the *substance*,

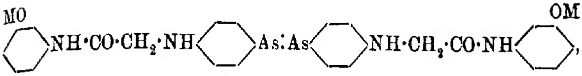
$$AgO\cdot C_6H_2Br_2\cdot AsO_3H_2,C_5H_5N,$$

m. p. 157—158°, in which the relative positions of pyridine and silver may possibly be reversed. When a solution of the sodium salt of 3:5:3′:5′-tetrabromo-*p*-arsenophenol is treated with silver nitrate, it gives a brown precipitate of *di-silver* 3:5:3′:5′-*tetrabromo*-p-*arsenophenoxide*, which dissolves in sodium hydroxide to a clear brown solution which closely resembles sodium silver salvarsan, but, on ultra-filtration, gives a black residue of colloidal silver and a colourless solution.

Arsenobenzene, conveniently prepared by the reduction of phenylarsinic acid with hypophosphorous acid, has m. p. 208°, whereas Michaelis and Schulte give m. p. 196°. When treated with silver nitrate, it becomes coated with a brownish-black deposit of silver, and is partly transformed into phenylarsinic acid; a somewhat similar phenomenon is observed with gold chloride, but it does not appear to react with copper chloride. H. W.

Aromatic Arsenical Compounds. WALTER ABRAHAM JACOBS, WADE HAMILTON BROWN, MICHAEL HEIDELBERGER, and LOUISE PEARCE (Brit. Pat. 128181; addition to Brit. Pat. 120385. Compare A., 1919, i, 231).—The sodium or potassium salts of the

N-(arsenoaryl)bis-α-aminoacylarylamides of the formula



where M is the alkali metal, previously described (*loc. cit.*), are equally valuable for the treatment of trypanosomal or spirochætal infection, and, being soluble in water, are particularly suitable for practical therapeutic use. As an example of their preparation, equivalent quantities of sodium hydroxide and *N*-(arsenophenyl)-bisglycyl-*m*-aminophenol may be dissolved together in water, and the salt isolated either by evaporating to dryness under reduced pressure or by precipitation with a liquid miscible with water, such as acetone or alcohol. It forms a yellow powder, readily soluble in water. G. F. M.

Physiological Chemistry.

The Equilibrium between Oxygen and Carbonic Acid in Blood. LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1920, **41**, 401—430).—This paper seeks to explain the interaction between oxygen and carbonic acid in blood by means of the theory of acid-base equilibrium. The isohydric change from fully reduced to fully oxygenated blood, the transfer of base from carbonic acid to hæmoglobin, which is the main feature of this process, and the change of strength, as acid, of a portion of the hæmoglobin molecule, which is its cause, are discussed. It is shown that all these phenomena can be explained by the assumption that a certain acid radicle of the hæmoglobin molecule has, for reduced hæmoglobin and oxyhæmoglobin, respectively, the following values: $K_R = 2\cdot3 \times 10^{-8}$, $K_0 = 2\cdot0 \times 10^{-7}$. From this consideration, it follows that the salt of the acid radicle in question must have a greater affinity for oxygen than the free acid. If the mass law constants of the reaction of salt and acid with oxygen were K_s and $K^{\cdot}$, respectively, it should be approximately true that $K_A/K_s = K_0/K_R = 9$. In the light of these considerations, the equilibrium between protein acid radicles and base in blood is examined. The bearings of these considerations on Hill's equation for the equilibrium between hæmoglobin and oxygen is considered, but at this point the difficulties are only partly overcome. The union of hæmoglobin as a base with acids, and especially with carbonic acid in blood, is discussed. Finally, the bearing of these considerations on the physiological processes, both the homogeneous reactions within the corpuscles and the plasma, and also the heterogeneous exchanges between corpuscles and plasma, is investigated.

J. C. D.

Alkalinity of Blood. RENÉ CLOGNE (*J. Pharm. Chim.*, 1920, [vii], **21**, 49—62).—See this vol., ii, 340.

The Colloidal Chemical Action of Normal Alkali Salts on the Process of Phagocytosis. W. RADSMA (*Arch. Néerland. Physiol.*, 1920, **4**, 197—215).—The influence of normal alkali salts on phagocytosis depends both on the cations and the anions. Arranged in descending order of intensity of phagocytosis, the anions are Cl', ClO_3', Br', NO_3', I', CNS', and the cations are $Na^{\cdot}$, $K^{\cdot}$, $Rb^{\cdot}$, $Cs^{\cdot}$, $Li^{\cdot}$, there being very little difference between corresponding salts of sodium, potassium, and rubidium. The action of these salts on the process of phagocytosis must be considered as a lyotropic action. The compounds formed between the protein substances of the protoplasm of the membrane of the leucocytes and the ions mentioned above play no direct part in the mechanism of phagocytosis. The point of action of the salt is not at the interior of the leucocyte, but in the protein substances at the surface of the leucocyte, and the intensity of the phagocytosis is an indicator of the colloidal chemical structure of the protein substances of the protoplasm at this surface. W. G.

Nutritive Value of the Proteins of the Barley, Oat, Rye, and Wheat Kernels. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 275—306).—The proteins of the entire kernel of these grains are adequate for the growth of albino rats, being more efficient for this purpose than the proteins of the endosperm alone.
J. C. D.

Studies in Nutrition. II. The Rôle of Cystine in Nutrition as Exemplified by Nutrition Experiments with the Proteins of the Navy Bean (Phaseolus vulgaris). CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1920, **41**, 379—389).—Cystine is essential for normal growth. Phaseolin, the principal protein of the navy bean, is rendered a more efficient food by heating with water. Cooked phaseolin or cooked navy bean, when supplemented with cystine, furnished adequate protein for normal growth. J. C. D.

The Influence of Radioactive Elements on the Development [of Tadpoles]. A. J. P. VAN DEN BROEK (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 563—567).—Tadpoles in a medium containing a radioactive substance antagonistic to potassium, namely, uranium, grow and metamorphose less quickly than in a medium only containing potassium. There is an indication that the presence of equi-radioactive quantities of the antagonistic substance tends to prevent the absorption of potassium by the tadpole, and there is also some indication of a poisoning effect. W. G.

Effect of the Chlorine Substitution Products of Methane, Acetaldehyde, and of Sodium Acetate on Catalase Production. W. E. BURGE and F. L. BURGE (*J. Biol. Chem.*, 1920, **41**, 307—314).—The inhibitory action of chlorine substitution products of methane on catalase action is proportionate to the degree of substitution. Similarly, chloral is more inhibitory than acetaldehyde. The ingestion of sodium acetate causes an increase of catalase, but this is less marked when sodium salts of the chloroacetic acids are used. The chlorine appears to decrease catalase by direct destruction and by decreasing the output from the liver. The increase in oxidation following the ingestion of glycine is attributed to an increase in catalase, whereas the decrease in oxidation during narcosis is attributed to a decrease in the enzyme.

J. C. D.

Influence of Uranium and Potassium on the Viscosity of Colloidal Liquids. I. GUNZBURG (*Arch. Néerland. Physiol.*, 1920, **4**, 233—242).—The viscosity of the muscular juice from a frog is above normal in liquids containing less than 25 mg. or more than 100 mg. of uranyl nitrate per litre, there being a point of minimum viscosity at a concentration of approximately 50 mg. of uranyl nitrate per litre. In the presence of potassium chloride, the viscosity remains almost constant at a value below normal for all concentrations of the chloride, although there is indication of a critical point at a concentration of 0·75—1·25 grams of potassium chloride per litre. In the presence of a mixture of the two salts, the viscosity of the muscular juice depends on the relative proportions of the two salts present.

W. G.

Genesis of Thiocyanic Acid in Animals. IX. SERAFINO DEZANI (*Arch. Farm. sperim. Sci. aff.*, 1919, **28**, 23—32. Compare this vol., i, 345).—The results of further experiments, together with those already described, lead to the final conclusion that thiocyanic acid is not produced in the animal organism, but is purely exogenetic.

T. H. P.

Chemistry of Vegetable Physiology and Agriculture

Biochemistry of the Acetone and Butyl Alcohol Fermentation of Starch by Bacillus Granulobacter Pectinovorum. HORACE B. SPEAKMAN (*J. Biol. Chem.*, 1920, **41**, 319—343).

Bacillus granulobacter pectinovorum growing in a medium rich in starch changes the latter into dextrose by exoenzymic activity. The dextrose then passes into the cell, and is oxidised to acetic and butyric acids, which are reduced in part to the corresponding alcohols.

J. C. D.

Fermentation of Lævulose by Lactobacillus pentoaceticus, N. Sp. W. H. PETERSON and E. B. FRED (*J. Biol. Chem.*, 1920, **41**, 431—450).—These organisms, which are closely related to the so-called "mannitol bacteria," will attack lævulose, with the production of acetic and lactic acids, mannitol, and carbon dioxide. As much as 30 to 40% of the lævulose may be converted into mannitol in the early stages of the fermentation, but if the process is allowed to go on for a long time, this product is slowly attacked, with the formation of acetic and lactic acids. The same organisms will decompose calcium and sodium malates, with the formation of carbon dioxide and lactic and acetic acids. It is suggested that malic acid may be an intermediate product in the fermentation of the lævulose. J. C. D.

Chemistry of Alcoholic Fermentation. CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, **53**, [*B*], 462—469).—The results obtained recently by Zerner (this vol., i, 350) are in general agreement with the older data of Neuberg and his co-workers. Zerner however, attributes the impossibility of effecting complete conversion of sugar into glycerol and acetaldehyde to a comparatively slow union of the latter with the bisulphite; the work of Kerp shows, on the other hand, that the union is rapid, whilst, in addition, the importance of the development of alkali hydroxide ($Me{\cdot}CHO + Na_2SO_3 + H_2O = Me{\cdot}CH(OH){\cdot}O{\cdot}SO_2Na + NaOH$) has been completely overlooked. Further, Zerner's conclusion that pyruvic acid cannot be the preliminary stage in the formation of acetaldehyde is based on an erroneous interpretation of an unsuitably devised experiment; absence of evolution of carbon dioxide from a fermenting solution of potassium pyruvate in the presence of a molecule of normal sodium sulphite is to be expected, since reaction occurs in accordance with the scheme $COMe{\cdot}CO_2K + Na_2SO_3 + H_2O \longrightarrow OH{\cdot}CHMe{\cdot}O{\cdot}SO_2K + Na_2CO_3$. The action is also complicated by the fact that fermentation occurs within the living yeast cell, which is now shown to be impermeable to normal sodium sulphite, so that the union of the latter with the aldehyde must occur outside the cell. H. W.

The Biochemical Production of Pyruvic Acid. A. FERNBACH and M. SCHOEN (*Compt. rend.*, 1920, **170**, 764—766. Compare A., 1913, i, 231; 1914, i, 237, 910).—Further evidence is given of the formation of pyruvic acid by yeast during alcoholic fermentation. An essential condition for its production is that the medium should be kept neutral, which is best done by the addition of calcium carbonate. Thus, by a change in the reaction of the medium, a change is produced in the nature and relative proportions of the products formed. The formation of pyruvic acid also requires that the medium shall be an inorganic one. W. G.

The Significance of the Peroxydase Reaction with Reference to the Viability of Seeds. J. S. MCHARGUE (*J. Amer. Chem. Soc.*, 1920, **42**, 612—615).—Although it has been suggested

that tissues or organs are dead if they fail to show the reactions of peroxydases and oxydases, the author has observed that dead grains, for example, lettuce seed, which failed to give the former reaction, contained a catalase which decomposed hydrogen peroxide; but evidence is adduced to show that the peroxydase reaction is only given by viable seed, and that the intensity of the reaction can be used to distinguish between seeds of low, medium, and high viability. The reaction failed with samples of corn, hemp seed, tomato seed, tobacco seed, oats, cowpeas, soja beans, castor beans, and lettuce seed, which all showed zero germination. Moreover, the temperature at which the blue colour disappeared increased with viability of the seed, although it varied somewhat with the species. Further, the peroxydase reaction was given by the germ, but not by the endosperm, of corn; but when the separation and grinding preparatory to the test were performed under water or alcohol, the germs also gave only a faint reaction, showing that they contain a substance, presumably an oxygenase, which, on exposure to air, rapidly absorbs oxygen, forming the peroxydase. Of the twenty species examined, only soja beans, lucerne, and lettuce seeds contained both oxydases and peroxydases; the respective reactions in each case were both pronounced, weak and strong, intense and moderate. J. K.

Carbon Monoxide a Product of Respiration. SETH C. LANGDON and WALTER R. GAILEY (*J. Amer. Chem. Soc.*, 1920, **42**, 641—646).—The conditions under which carbon monoxide is produced in the pneumatocyst (floater) of the giant Pacific Coast kelp, *Nereocystis leutkeana* (A., 1917, i, 372), have been more closely examined. It is not a result of decay or due to the action of enzymes, because finely ground kelp in contact with sea-water gives carbon dioxide and hydrogen only. When the lower part of the stipe was cut away, and the upper part closed with a cork and suspended in the sea after being filled with a gas of known composition, the plant continued to live and grow. When air was used, carbon monoxide was produced, irrespective of whether the fronds had been removed or not, or whether the plant was kept in the light or in the dark, and whatever sections of the stipe were employed. With nitrogen or hydrogen, however, no carbon monoxide was produced, but several per cent. of carbon dioxide were produced. Finally, carbon monoxide was only generated in the living plant. It is therefore considered to be a respiration product rather than an intermediate product in photosynthesis. J. K.

Influence of the Pyrrole Nucleus in the Formation of Chlorophyll. II. B. ODDO and G. POLLACCI (*Gazzetta*, 1920, **50**, i, 54—70. Compare A., 1915, i, 1083).—Previous publications on this subject having been discussed, the preparation of magnesium pyrrole-2-carboxylate, and experiments on the influence of nutrient solutions containing this compound on the growth of various plants, are described.

Magnesium pyrrole-2-carboxylate, $\left[\begin{matrix}CH\text{-}CH \\ CH\cdot NH\end{matrix}\!>\!C\cdot CO_2\right]_2 Mg,2H_2O$, obtained by heating an aqueous-alcoholic solution of pyrrole-2-carboxylic acid (2 mols.) with magnesium oxide (1 mol.), crystallises in brush-like aggregates of needles or stellar aggregates of leaflets, and begins to decompose at about 260°.

The culture experiments were made with *Zea maïs*, *Solanum nigrum*, *Datura stramonium*, *Euphorbia* sp., and *Aster sinensis*, the culture liquids containing calcium nitrate, ammonium sulphate, potassium nitrate, and potassium dihydrogen phosphate (or magnesium pyrrole-2-carboxylate), all carefully purified from traces of iron. The results show that, in the nutrient solutions containing the pyrrole compound, the plants exhibit normal growth, whereas in those free from this compound, plants are obtained with leaves showing marked chlorosis.

Thus, plants grown in a nutritive medium containing an assimilable pyrrole derivative form chlorophyll, even in absence of iron. When no such pyrrole derivative is present, iron constitutes an indispensable element in order that the plastids may become green, and acts, indeed, as a catalyst in the formation of the pyrrole nucleus, which constitutes the centre of the whole chlorophyll complex. Pyrrole and magnesium are, then, the substances which cause plants to become green. T. H. P.

Influence of certain Organic Compounds on the Development of Plants. IV. G. Ciamician and C. Ravenna (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 7—13. Compare A., 1919, i, 241).—Further experiments have been made with bean plants watered with 0·1% solutions of various compounds. Of the normal amines, methylamine is the least toxic, whilst the toxicity diminishes continuously in passing from ethylamine to *n*-amylamine; the action is manifested by the appearance of yellow, translucent spots on the leaves, the plants being killed by ethylamine and rendered less vigorous by the other amines. *iso*Amylamine is somewhat more poisonous than *n*-amylamine, and determines a characteristic albinism of the compound leaves, which are deprived of chlorophyll either entirely or everywhere but along the principal veins; this albinism recalls that due to nicotine, which is accompanied by *iso*amylamine in tobacco. Potassium *n*-butyrate is without apparent effect, whereas the *iso*butyrate causes partial falling of the leaves.

Formamide causes fall of the seed-leaves, probably owing to the presence of the aldehydic group, whilst acetamide is completely innocuous. Oxalic acid causes less vigorous growth than succinic acid. Methyl and, especially, ethyl tartrates produce on the seed-leaves translucent spots, which lead to slow desiccation of the plants. Pyridine allows the plants to develop normally, but picoline produces yellow spots on both the seed-leaves and the compound leaves, without, however, injuring the plants seriously. The influence of the introduction of methyl groups into a molecule

is exhibited more markedly with derivatives of piperidine, which itself is only slightly toxic, whereas 1-methylpiperidine and coniine are highly toxic. Quinoline, *iso*quinoline, and 2-methylquinoline are all intensely toxic, the last more so than the first two, the effects of which are equal. Cocaine kills the plants, ecgonine and the methyl ether of norecgonine produce brown spots on the seed-leaves, but do not prevent further development, although with the former this is restricted; norecgonine produces no apparent effect. Unlike tetramethylammonium salts, betaine is only slightly toxic, producing merely partial withering of the seed-leaves.

With broad bean, pumpkin, and tomato plants, less marked effects are obtained than with beans, but those substances which act most intensely on the latter affect these three plants similarly.

Certain substances, especially morphine and catechol, give an exceptionally dark green colour to the leaves, but the absorption spectra of alcoholic extracts of such leaves exhibit no qualitative difference, but only a different intensity of absorption from those obtained with normal leaves; photometric measurements indicate the presence of twice as much chlorophyll in the former as in the latter leaves, but the proportion of starch present is no greater. Thus the quantity of starch present is not related to the intensity of the green colour of the leaves, and although most of the toxic substances examined favour the deepening of the colour, some, such as theobromine, produce the opposite effect.

The toxic substances investigated do not merely act on the roots, but pass into the tissues of the plant. With catechol, however, no trace is detectable in the plant, this compound being probably destroyed by enzymic action (compare A., 1918, i, 93).

T. H. P.

The Lipolytic Activity of the Castor and Soja Bean. ARTHUR WILLIS BARTON (*J. Amer. Chem. Soc.*, 1920, **42**, 620—632).—Preliminary to a study of the activity of the lipases of castor and soja beans, it was shown that Falk's method of determining the liberated fatty acids (A., 1912, i, 522) is inapplicable when lard or olive oil is used as a substrate; complete neutralisation is only achieved by the addition of alcohol and ether to produce a homogeneous solution before titration with aqueous alkali hydroxide. In the case of castor beans, the husks were removed for the preparation of the lipase, because its activity was in this way doubled, but this was unnecessary with soja beans. From his results the author deduces that (1) castor bean lipase is more intense in its action than soja bean; (2) the ranges of acidity of medium in which action on lard and olive oil takes place are practically the same for the two lipases (0·0—0·5% hydrochloric acid), and are independent of the substrate; (3) the degree of activity for a given acidity is practically the same for olive oil and for lard, the maximum for castor bean being at 0·2% and for soja bean at 0·4%; (4) the activity towards ethyl butyrate is less, and the range of acidity in which

action takes place is much higher and shorter. It is concluded that soja and castor beans contain more than one, but the same, lipases.

J. K.

Proso Millet—Analysis of the Oil—a Characteristic Alcohol. B. A. DUNBAR and E. R. BINNEWIES (*J. Amer. Chem. Soc.*, 1920, **42**, 658—666).—The oil extracted from proso millet, *Panicum miliaceum*, by ether or light petroleum gradually deposits thin, pearly-white plates, m. p. 279° (corr.), soluble in most organic solvents, but sparingly in cold ether or alcohol. As it could not be identified, it was called "*prosol.*" It has the formula $C_{24}H_{36}O_2$, can be acetylated, and with hydroxylamine gives an unsatisfactory quantity of a precipitate, presumably an oxime. The formation of a fluorescein, under conditions vaguely specified, is looked on as evidence of a ring structure, with two side-chains in the ortho-position. The oil itself is a semi-drying oil, comparable with rape-seed oil. [For analytical details, see *J. Soc. Chem. Ind.*, 1920, .]

J. K.

Chemical Examination of the Root of Nerium Odorum (Kanher). SHUNKER TRIMBAK GADRE (*J. Ind. Inst. Sci.*, 1916, 1, 181—199).—The air-dried roots of *Nerium Odorum* collected in winter in the Krishna valley, when extracted with hot alcohol, lost 13·7% of their weight. The alcoholic extract, when distilled in steam, yielded a small amount of an orange-coloured essential oil, having D_4^{30} 0·8660; $[\alpha]_D^{31}$ −4·088°; n_D 1·40315. Of the total residual extract, 45% was soluble in water, and this aqueous solution contained a small amount of a crystalline phenolic compound, m. p. 140—141°, a considerable amount of a glucoside, and free dextrose. The portion of the extract insoluble in water, constituting 7·5% of the original root, was composed of a hard and a soft resin. From the hard resin the author isolated formic and butyric acids in traces, oleic, linolic, palmitic and stearic acids, a new alcohol, *kanerol*, $C_{30}H_{50}O$, m. p. 185·7—186·2° (corr.), $[\alpha]_D^{30}$ +80·1°, giving an *acetyl* derivative, m. p. 208—210°, $[\alpha]_D^{30}$ +84·88°, and a *benzoyl* derivative, m. p. 189—190°. In addition, the hard resin contained a small quantity of an aromatic acid, m. p. 243—245°. The soft resin contained oleic, linolic, palmitic and stearic acids, and the alcohol kanerol, which gave the colour reactions for a phytosterol, and in most respects closely resembled α-amyrin.

The ethyl acetate and the alcohol extracts of the hard resin were found to consist mainly of resin acids.

W. G.

Okra Seed Oil. GEORGE S. JAMIESON and WALTER F. BAUGHMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 166—170).—The chemical characteristics of four samples of the cold-pressed oil from okra seed (*Abelmoschus esculentus*, Malvaceæ) have been determined. These oils vary somewhat in composition. A recently expressed oil contained the glycerides of palmitic acid (27·23%), stearic acid (2·75%), arachidic acid (0·05%), oleic acid (43·74%), linolic acid (26·62%), and unsaponifiable matter (0·37%).

H. W.

Pimpernel Saponin. CONRAD VESTLIN (*Pharm. Zentr.-h.*, 1920, **61**, 77—78).—Roots of *Pimpinella saxifraga germ.*, yielded 1·107% of a saponin having the formula $C_{23}H_{36}O_{18},2H_2O$.
W. P. S.

Hydrocyanic Acid Content of Phaseolus lunatus. II. H. LÜHRIG (*Chem. Zeit.*, 1920, **44**, 262. Compare this vol., i, 359).—Further experiments on hydrocyanic acid in *Phaseolus lunatus* beans showed that treatment of the beans with saliva did not increase the amount of hydrocyanic acid above that formed by the action of the natural enzyme of the beans; prolonged action of saliva tended to reduce the amount of hydrocyanic acid. The residues remaining after the removal of the hydrocyanic acid by distillation were treated with emulsin, saliva, bile, and pancreatic juice, but no further amount of hydrocyanic acid was obtained.
W. P. S.

Urease of the Seeds of Robinia pseudacacia. P. Y. YI (*Ber. deuts. pharm. Ges.*, 1920, **30**, 178—191).—The quantity of ammonia liberated in the enzymic decomposition of urea by the powdered seeds of *Robinia pseudacacia* increases proportionately with the amount of seed powder used and the duration of the action, and the decomposition is accelerated by raising the temperature to 37°. The most active preparations of the urease are obtained by precipitation with alcohol from an aqueous extract of the seeds, although this causes some injury to the enzyme. Lead acetate, sodium chloride, and ammonium sulphate are still less suitable precipitants. When salt solutions of equal concentration are used, the most energetic action on urea is obtained with sodium acetate solution. Pure water dissolves most urease at 40°, the activity of the aqueous solutions decreasing with the rise in temperature, and practically ceasing at 80°. The fact that the urease of *Robinia* seeds is only partly soluble in water supports the view that two or more ureases differing in physical properties are present. *Robinia* urease decomposes *as*-dimethyl- and diethylcarbamides, but has little, if any, action on the corresponding symmetrical compounds. C. A. M.

The Hydrocyanic Acid Question. IV. The Seeds of Schleichera trijuga. L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1920, **58**, 17—20; from *Chem. Zentr.*, 1920, i, 338. Compare this vol., i, 130).—Uncombined hydrocyanic acid is not present in the seeds of *Schleichera trijuga*, Willd.; a compound of it, however, can be removed from the oil with ether or light petroleum, which is not identical with amygdalin, phaseolunatin, or linamarin. It does not appear to be a glucoside, but is possibly a hydroxynitrile.
H. W.

The Function of Vitamines in the Metabolism of Sclerotinia cinerea. J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 549—585).—The solutions found by Currie (A., 1917, i, 614) to promote the growth of *Aspergillus niger* failed when

applied to the case of *Sclerotinia cinerea* (Bon.), Schröter, the brown rot organism of peaches and plums, but normal development took place when small amounts of peach, prune, or apple juice were added, that of the first being most effective. A variety of nitrogen compounds, sugars, pectin, and salts of organic and inorganic acids were also ineffective when not contaminated with mother liquors from a plant juice. It is therefore suggested that the vitamines present in the juices are responsible for their influence.

By means of adsorption with fuller's earth, vitamine preparations were made from many and most varied sources, both plant and animal. All these preparations were active in promoting growth of *Sclerotinia*; a few of them also promoted reproduction.

Some experimental evidence was obtained favouring the view that there might be two separate vitamine factors involved in the two phases, vegetation and reproduction, but, on the other hand, the hypothesis of but a single vitamine for *Sclerotinia* is more plausible and accords with much of the experimental evidence, and it is very probable that reproduction in *Sclerotinia* is simply a different manifestation of the same activities as characterise vegetation. The *Sclerotinia* vitamine is possibly identical with water-soluble *B* of the higher animals. J. K.

Composition of Hubbard Squash Seed Oil. WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1920, **42**, 152—157).—The seeds of *Cucurbita maxima* contained 5·72% of moisture and 36·66% of matter soluble in ether. The cold-pressed oil had D_{25}^{25} 0·9179, n^{25} 1·4714, iodine number (Hanus) 121·0, saponification number 191·5, Reichert-Messel number 0·37, Polenske number 0·39, acetyl number 27·8, acid number 0·50. Chemical examination showed the presence of the glycerides of palmitic acid (13%), stearic acid (6%), arachidic acid (trace, about 0·04%), oleic acid (37%), and linolic acid (44%). The unsaponifiable matter amounted to 1%. H. W.

Nicotine in Tobacco: Genesis and Function of Alkaloids. LUIGI BERNARDINI (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 62—66).—The results of the author's experiments are as follows. Nicotine is not present in the seed of the tobacco plant, and is harmful to its germination, as also are larger doses of other compounds which contain heterocyclic nuclei and are related chemically to nicotine, such as pyridine and picoline. The alkaloid appears in the young plant immediately the chlorophyll begins to function, and originates in the leaves. The plant, which in its normal development contains the nicotine in its elaborating organs in virtue of the greater vital activity there developed, responds to any serious traumatic lesion, such as cutting, which attacks it at an important stage of its vegetative cycle, the alkaloid being thereby produced in increased quantity and localised in the regions adjacent to the lesion. The localised nicotine of the roots, and especially that accumulated in the leaves, is not utilised by the

plant even when the latter is placed in conditions favourable to such utilisation.

These results lead to the assumption that the nicotine, probably formed from certain residues of the nitrogen katabolism, is elaborated by the plant in order either to prevent accumulation of such residues in the organism or to utilise them, with intensification of their harmfulness, in defence of its organs. An analogous case is that of tannin, which is elaborated by plants to prevent accumulation of polyhydric phenolic residues; the tannin is perhaps more injurious than these residues, but it may be utilised by the plant, being localised, by a simple mechanism, in the wood for its formation and preservation. T. H. P.

Urea and other Sources of Nitrogen for Green Plants. T. Bokorny (*Pfluger's Archiv*, 1918, **172**, 466—496; from *Physiol. Abstr.*, **4**, 57).—Green plants are capable of disintegrating and utilising almost as many organic substances as the fungi are. Urea in an initial concentration of 0·05% has a beneficial action on the germination of wheat, and acts as nutrient to the seedlings. 0·1% has a harmful action. J. C. D.

Effect of Lime on the Sodium Chloride Tolerance of Wheat Seedlings. J. A. LeClerc and J. F. Breazeale (*J. Agric. Res.*, 1920, **18**, 347—356).—As a result of water culture and sand culture trials with wheat seedlings, it is shown that very small amounts of calcium oxide or sulphate overcome the toxic effects of sodium chloride or sulphate. Magnesium sulphate and barium chloride are slightly antagonistic to sodium chloride, but potassium chloride, sodium nitrate, sodium phosphate, ferric chloride, and alum have no effect on the toxicity of sodium chloride.

Under the experimental conditions, the presence of lime did not prevent the entry of sodium ch'oride or sulphate into the plant, the antagonistic effect of lime not being due, apparently, to its effect on the permeability of the cells, but to some other cause.

The higher tolerance to alkali salts shown by plants in soil or sand cultures as compared with those grown in water cultures is not due entirely to the physical effects of the presence of solid particles of different degrees of fineness, but also to certain soluble substances which are sometimes present in very small quantities. W. G.

Enzymes. III. Invertase and other Enzymes of Germinated Barley. D. Maestrini (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 509—511. Compare this vol., i, 273).—Germinated barley dried at temperatures below 40° contains invertase, extractable by 0·003 mol. % acetic acid solution, and present, not only in the emulsion, but also in the filtrate of the extract; the enzyme acts best at about 50°, and is destroyed at 55°. The extract of the germinated barley contains no maltase, lactase, or rennase, the coagulation of milk produced by the extract being due solely to the acidity of the latter, as it is effected even by the boiled extract. A catalase and an oxydase are, however, present in the germinated barley. T. H. P.

Constituents of Protein in Polished Rice. JUNZO KUROSAWA (*J. Tokyo Chem. Soc.*, 1919, **40**, 551—561).—In connexion with the nutritive value of various proteins, the nature of the rice protein has been reinvestigated. Dry, pure, polished rice contains 1·77% of total nitrogen, 1·14% of protein nitrogen, 0·13% of non-protein nitrogen, and 7·125% of total protein (=protein nitrogen × 6·25). The protein nitrogen contains 97·82% soluble in hot hydrochloric acid, 97·81% soluble in hot 30% sulphuric acid, 3·58% of humin (I) nitrogen, 9·20% of ammonia nitrogen in sulphuric acid, 1·18% of humin (II) nitrogen, 20·40% of nitrogen precipitated by acid, and 63·12% of other nitrogen in sulphuric acid. Of the total nitrogen, 10·89% is attributable to arginine, 8·89% to histidine, and 2·67% to cystine; these amounts are quite different from those recorded by other investigators. Cystine corresponds with 0·87%, tyrosine with 3·51%, and tryptophan with 0·88%, calculated on the dry material.

Matsui's observation is confirmed that guanidine nitrogen is eliminated in the Van Slyke method if the reaction is allowed to proceed for several hours. CHEMICAL ABSTRACTS.

Enzyme Action. XVIII. The Saccharogenic Actions of Potato Juice. GRACE MCGUIRE and K. GEORGE FALK (*J. Gen. Physiol.*, 1920, **2**, 215—227. Compare A., 1919, i, 426).—The marked action of the juice alone and also in the presence of added starch at p_H 4 to 5 is due to the hydrolysis of sucrose or raffinose by the sucrase present. There is very little degradation of starch. At p_H 6 there is action both on the part of the sucrase and the amylase, whilst at p_H 7 to 8 the action of the amylase is alone observable. J. C. D.

Nutritive Factors in Plant Tissues. III. Further Observations on the Distribution of the Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 451—468).—An attempt to place our knowledge of the value of certain foodstuffs as sources of the accessory factors on a quantitative basis. Lucerne and clover are extraordinarily rich in water-soluble *B*. Of the ordinary vegetables, tomatoes appear to be richest, whilst spinach, cabbage, turnip, and carrot are not quite so potent. The beetroot is not equal in this respect to the other roots tested, and Timothy hay also proved disappointing. The potato is evidently rich in the water-soluble *B* factor, which does not appear to be concentrated to any extent in the surface layers. No differences were noted in the food value of old and new potatoes. J. C. D.

Salt and Alkaline Soils. Origin of Sodium Carbonate in Soils. A. DE DOMINICIS (*Staz. sperim. agrar. Ital.*, **51**, 103—161; from *Chem. Zentr.*, 1918, ii, 982—983).—In considering the problem of irrigation of southern soils, account must be taken of

the relationship between irrigation, movement, distribution, and transformation of the neutral sodium salts. Incautious irrigation frequently defeats its purpose, since it results in raising the subterranean salt water, concentration of the salts in the surface layers, and formation of sodium carbonate instead of neutral salts; the occurrence of the carbonate renders the soil less fit for cultivation than does that of neutral salts. The carbonate can be removed by simple washing with water, but this involves the loss of all colloidal mineral and organic substances. Double decomposition between sodium chloride or sulphate and calcium carbonate plays little, if any, part in the production of sodium carbonate. This is shown by the fact that the presence of sodium chloride and sulphate hinders the formation of the carbonate, the latter only appearing after removal of the neutral salts, and being formed to a greater extent in proportion as the removal is more thorough. Nevertheless, an alkaline soil is indirectly dependent on a salt soil. The phenomenon is explained by Gedroiz on the assumption that sodium chloride and sulphate form peculiar compounds in the soil, which can only enter into reaction after removal of the salts to which they owe their origin. These are regarded as absorption compounds, and as being formed by double decomposition between absorbed substances, such as compounds of calcium and magnesium and sodium chloride and sulphate. The extent of the formation of sodium carbonate depends on the intensity and length of action of the neutral salts and on the content of adsorbed sodium which can be extracted with 10% hydrochloric acid.

The author's experiments lead him to a quite different conception of the action. The alkalinity depends primarily on absorbed sodium, but results from the hydrolysis of the "absorbates" when they leave the state of coagulation; the sodium hydroxide so formed can then react with calcium carbonate, but, more commonly, is converted into sodium carbonate by carbon dioxide. Actually, an alkaline reaction can be observed in the absence of calcium carbonate and carbon dioxide. The part played by the neutral salts consists in holding the absorbates in a coagulated condition, in which they are not hydrolysed. The action of gypsum in improving an alkaline soil does not consist in simple neutralisation of sodium carbonate. The carbonate and bicarbonate derived from it, together with the excess of gypsum, coagulate the colloids and change them again into calcium adsorbates, the action being facilitated by the presence of neutral sodium salts. The latter can themselves act helpfully in the removal of alkalinity, but only indirectly and in virtue of the corresponding anions. The prescribed irrigation with salt water is dangerous for the soil, since it inhibits the formation of sodium absorbates; the danger could, however, be avoided by simultaneous treatment with gypsum.

Organic compounds play a part in the formation of sodium carbonate in the soil. Among colloidal mineral substances, those of zeolitic nature, which by double decomposition can yield absorbents, are active; of these, the chabasite type, corresponding with

aluminium silicate, is the most important, whilst substitution occurs very slowly and dissociation takes place with greater difficulty with substances of the natrolitic type. H. W.

Absorption of Lime by Soils. F. J. WARTH and MAUNG PO SAW (*Mem. Dept. Agric. India*, 1919, **5**, 157—172).—A study of the absorption by different types of soils of calcium carbonate from solutions of calcium hydrogen carbonate at different concentrations and in the presence of varying amounts of carbon dioxide. On the results, a method for estimating the lime requirements of a soil is based and described. W. G.

The Action of Lime in the Soil. JOHN HUGHES (*J. Bath & W. & S. Co. Soc.*, 1919, [v], **13**, reprint, 10 pp.).—A study of the rate of carbonation of calcium oxide when mixed with four times its weight of soil (*a*) in the air-dry state, (*b*) kept moist with water and placed outdoors. Two types of soil were used, one containing 3·85% and the other 14·97% of organic matter and combined water. In both soils, which were exposed to the air in a moist state, the whole of the calcium oxide was carbonated within six weeks. The author discusses the results of Voelcker's experiments carried out at Woburn on the lime-magnesia ratio in soils. The lime and magnesia contents of eleven Herefordshire soils are given, and in all cases where the magnesia was in excess of the lime, full-crop results were not obtained. W. G.

The Relation of certain Acidic to Basic Constituents of the Soil affected by Ammonium Sulphate and Sodium Nitrate. L. P. HOWARD (*Soil Sci.*, 1919, **8**, 313—321).—The soils used were from permanent experimental plots which for the last twenty-five years have received, respectively, ammonium sulphate and sodium nitrate, half of each plot being limed. An exchange of bases, produced by treatment of the soil with a solution of potassium chloride, showed a marked degree of reserve acidity from the unlimed soil receiving ammonium sulphate. This acidity, so developed, showed a correlation with the acidity of an aluminium salt equivalent in amount to the weight of aluminium found in the extract. Digestion with hydrochloric acid showed that the quotient obtained by dividing the sum of the weights of the oxides of aluminium and iron by the sum of the weights of the oxides of calcium and magnesium ranged from 85 in the case of the unlimed soil receiving ammonium sulphate to 10 where lime and sodium nitrate were applied. Thus in these acid unlimed soils, iron and aluminium partly took the places occupied by calcium and magnesium in the limed soils. The soil solution acts as a buffer solution containing phosphates and carbonates, and the hydrogen-ion concentration in the soil solution from the unlimed plot receiving ammonium sulphate was very similar to that produced by the addition of even quite large amounts of aluminium salts to buffer solutions. W. G.

General and Physical Chemistry.

Perturbation Theory of the Helium Atom. A. LANDÉ (*Physikal. Zeitsch.*, 1920, **21**, 114—122).—A purely mathematical paper, deducing the series spectra of helium by the consistent application of the quantum theory to a system of two electrons revolving round a nucleus of charge $+2e$ in circular and elliptical paths, co-planar and inclined. F. S.

The K-Absorption Bands of Rare Earths for X-Rays. M. DE BROGLIE (*Compt. rend.*, 1920, **170**, 725).—The author has obtained the K bands for the elements numbered 69, 70, 71. The band of lutecium is placed between the two groups K_a and K_β of tungsten. Approximate measurements give the K band of thulium ($N=69$) at $\lambda=0{\cdot}208\times10^{-8}$, of neoytterbium ($N=70$) at $\lambda=0{\cdot}2015\times10^{-8}$, and of lutecium ($N=71$) at $\lambda=0{\cdot}195\times10^{-8}$. W. G.

The Constitution of Atmospheric Neon. F. W. ASTON (*Phil. Mag.*, 1920, [vi], **39**, 449—455).—The observation in 1912 by Sir J. J. Thomson of a faint but unmistakable parabola corresponding roughly with an atomic weight 22, in addition to the expected one at 20, in the positive ray spectrum of neon, and the absence of any parabola at 22 except in presence of neon, was strong evidence of the line being due to an isotope of neon. Fractional distillation failed to effect any separation, and diffusion results, although more hopeful, have failed to be conclusive. A difference of 0·7% in density in the first set of experiments could not be repeated in more elaborate ones, 0·3% difference only being obtained. By new and refined methods of positive-ray analysis, exact measurements have shown that the atomic weight of the two constituents in neither case corresponds exactly with that of neon, 20·2. Four parabolas corresponding with the doubly and singly positively charged atoms of the two isotopes have been carefully measured. The corrected results gave for the one constituent (Ne^{α}) an atomic weight of 20·00, and for the other (Ne^{β}) 22·00, to an accuracy of about 0·1%. The intensities of the lines were in agreement with the required 90% to 10% ratio. On the clearest spectra there was evidence of a third isotope of mass 21, extremely faint, and probably not present to the extent of 1%. F. S.

Radioactive Disintegration Products in the Free Atmosphere and the Probability of their Origin being the Sun. HERMANN BONGARDS (*Physikal. Zeitsch.*, 1920, **21**, 141—145).—The radioactivity of a wire suspended at a mean height of 1500 metres, under the influence of the earth's field, has been determined. It is shown that a relationship exists between the activity,

the air pressure at the earth's surface, and the potential temperature in the air layer between 1000 and 2500 metres. A well-defined parallelism is observed between the activity and the temperature in this air layer. The temperature changes are regarded as the cause of the pressure changes. Since the influence of the radioactive substances on the temperature cannot occur to the observed extent, and since temperature is without influence on the activity, it is assumed that a radiation of material from a definite and restricted portion of the sun is the cause of the observed effects. This radiated matter carries with it the emanation particles which are observed in the atmosphere. The heat action of the material radiations constitutes the chief source of heat of the higher layers of the atmosphere. J. F. S.

Intermolecular Change of Place of Similar Atoms. GEORG VON HEVESY and LÁSZLÓ ZECHMEISTER (*Ber.*, 1920, 53, [*B*], 410—415. Compare von Hevesy and Rona, A., 1915, ii, 247). —By employing radioactive methods, the authors show that intermolecular change of place occurs between lead atoms to an extent which can be exactly calculated from the law of probability when they are in an ionised state; organically combined lead atoms are not subject to similar transposition in homogeneous phase. Thus, when activated lead nitrate and inactive lead chloride are dissolved in molar proportions in boiling pyridine, and the solution is kept hot for some time and then allowed to cool, the lead chloride which separates is found to be exactly half as radioactive as the original specimen of lead nitrate. Similar results are obtained with the following pairs of compounds: lead formate (active) and lead acetate in water; plumbous acetate (active) and plumbic acetate in glacial acetic acid; plumbic acetate (active) and plumbous acetate in glacial acetic acid. Interchange does not occur with lead chloride (active) and lead tetraphenyl in pyridine, with lead acetate (active) and lead tetraphenyl in amyl alcohol, or with lead nitrate (active) and lead diphenyl nitrate in dilute ethyl alcohol. H. W.

Radioactivity of the Rocks of the Kolar Gold Fields. HERBERT EDMESTON WATSON and GOSTABEHARI PAL (*J. Ind. Inst. Sci.*, 1914, 1, 39—46).—The Kolar goldfields on the Mysore plateau are worked to a depth of 1100 m., and the rock consists of schists of very uniform character. The rocks were fused with potassium hydroxide in a copper flask under reduced pressure, and the radium emanation found to be liberated as completely as at the higher temperature required for fusion with alkali carbonates. Some nearly pure hydrogen is liberated, which causes the readings in the electroscope to be low, and it was eliminated by passing the gas over red-hot copper oxide before introducing it into the electroscope. The mean quantity of radium in the schists was found to be 0·19 [$\times 10^{-12}$ gram of radium per gram of rock], the quantity varying but little with depth. These rocks, which are

probably the oldest known, contain as little radium as any yet examined, and the temperature gradient in the mines is abnormally small. Other specimens of rocks of later date contained larger amounts of radium, from 0·8 to 6·9. F. S.

Radioactivity and Life. H. ZWAARDEMAKER (*Arch. Néerland. Physiol.*, 1920, **4**, 177—196).—A general discussion of work already published (compare A., 1917, i, 241; 1918, i, 326; ii, 182). W. G.

The Cathode Fall. I. In Neon and Helium. H. E. WATSON and G. R. PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 143—165).—From Aston's results (*Proc. Roy. Soc.*, 1911, **84**, 526), the cathode fall should be equal to the total difference of potential across the electrodes when the anode is situated in the negative glow. A systematic investigation has been made of the requirements necessary to obtain trustworthy results by this method. Using a cylindrical tube with plane parallel electrodes 7·2 cm. in diameter, the same diameter as the tube, the minimum cathode fall was found to be constant to 1 volt over a wide range of pressure—185 volts between 6 and 16 mm. for copper electrodes in neon—while the current was passing. The laws governing the relations between the cathode fall, the gas pressure, and the current were found to agree with those found by other observers using exploring wires. The cathode fall was determined in very pure helium and neon for twenty-four different metals as cathodes, and with few exceptions were all within 5% of 145·5 volts for neon and 155·5 for helium. F. S.

The Cathode Fall. II. In Argon, Hydrogen, and Nitrogen. GOPAL PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 166—177). —The cathode fall for twenty different metals in argon, nitrogen, and hydrogen has been determined, and in any one gas found to be nearly, but not exactly, the same for all metals. The differences in different gases for the same metal were nearly all independent of the metal, but the results in hydrogen were irregular. Nitrogen behaved very similarly to the monatomic gases.
F. S.

Electrical Conductivity in Solid Crystallised Compounds. I. Verification of Faraday's Law in the Electrolysis of Solid Salts of Heavy Metals. C. TUBANDT and SOPHIE EGGERT (*Zeitsch. anorg. Chem.*, 1920, **110**, 196—236).—One of the most important difficulties encountered in the practical determination of the conductivity of solid salts and the verification of Faraday's law for such conductors is the short-circuiting brought about by the formation of a bridge of metal, formed by the electrolysis of the salt, between the anode and the cathode. The metal is deposited in the form of very fine threads or delicate, dendritic growths, which spread so rapidly across the electrodes that a

quantitative investigation of the electrolysis of the salt is impossible. It has been found that the cubic form of silver iodide, when electrolysed, using a silver anode and a platinum cathode, gives a deposit of silver at the cathode in the form of a perfectly coherent tree, the growth of which is so slow that there is no danger of short-circuiting. The hexagonal modification of silver iodide, stable below 144·6°, has a maximum specific conductivity of 0·00034, whilst the cubic modification has at the transition point the much greater value 1·31, which rises to 2·64 in the neighbourhood of the melting point, 552°. By carrying out the electrolysis of the salt at about 150°, using a current of 0·04 to 0·1 amp., a complete verification of Faraday's law was obtained, both the loss of silver from the anode and the weight deposited at the cathode agreeing within a fraction of 1% with the weight of silver deposited in a silver voltameter included in the circuit. The law was also verified for silver bromide, chloride, and nitrate by interposing a layer of silver iodide between the cathode and the salt under examination, the iodide ensuring that the metal was deposited at the cathode in a coherent form. The electrolysis of lead chloride, bromide, and iodide was also investigated, using a silver anode and a platinum cathode. The loss of silver from the anode afforded a complete verification of the law, but owing to the dendritic form in which the lead was deposited at the cathode, no trustworthy results could be obtained from this side. In choosing the temperature at which to carry out the electrolysis, care had to be taken that no fusion occurred, and for this purpose the fusion diagrams for the systems $PbCl_2$–$AgCl$, $PbBr_2$–$AgBr$, and PbI_2–AgI were investigated experimentally. Silver and lead chlorides form a eutectic at 314°, containing 40 mols. % of lead chloride. Silver and lead bromides form a compound,

$$2PbBr_2,AgBr;$$

there are two eutectic points, the first at 276° with 46 mols. % of $PbBr_2$, this eutectic crystallising from mixtures containing 0—66·67 mols. % of $PbBr_2$, all other mixtures showing eutectic crystallisation at 295°. Silver iodide–lead iodide mixtures show eutectic crystallisation at 395° with 0—20 mols. % AgI. From this point up to 100% AgI, mixed crystals of the compound $4AgI,PbI_2$ with PbI_2 are formed, the lowest crystallising point being 344°. Experiments on the electrolysis of cuprous iodide were inconclusive, on account of the difficulty of preparing the compound in a satisfactorily pure condition. E. H. R.

Photochemical Cell with Complex Cyanides. S. Iimori (*J. Tokyo Chem. Soc.*, 1918, **39**, 1—13).—Platinum electrodes are immersed in solutions of complex cyanides (potassium nickel or potassium platinum), and one of the electrodes is exposed to light. This electrode becomes positive, whilst it became negative in the potassium ferrocyanide cells previously examined by the author. The current quickly decays when the circuit is closed through a high resistance. The author is of opinion that the *E.M.F.* pro-

duced with these complex cyanides is not of the same nature as that obtained in other solutions. CHEMICAL ABSTRACTS.

Electromotive Force of Alloys of Zinc and Cadmium with Tin, Lead, and Bismuth. PAUL FUCHS (*Zeitsch. anorg. Chem.*, 1919, **109**, 80—88).—The *E.M.F.* of elements composed of alloys of cadmium with tin, lead, and bismuth of various compositions as one electrode, cadmium sulphate solution and cadmium as the other electrode: alloy | N-$CdSO_4$ | Cd, have been measured; similar cells of the type: alloy | N-$ZnSO_4$ | Zn, in which zinc takes the place of cadmium in the alloy, have also been measured. The cells were measured in the presence of hydrogen, and only gave constant values after several days. The results confirm the views of Tammann (A., 1919, ii, 398) that the *E.M.F.* varies with the composition of the alloy only so long as one phase is present, that is, as long as the alloy is a solution or a single series of mixed crystals, but as soon as two phases appear, the *E.M.F.* is no longer dependent on the composition. J. F. S.

The Free Energy of Potassium Hydroxide in Aqueous Solution and the Activities of its Ions. MING CHOW (*J. Amer. Chem. Soc.*, 1920, **42**, 488—497).—Experiments were made to determine, by means of electromotive force measurements, the free energy attending the transfer of potassium hydroxide in aqueous solution from one concentration to another, and from the free energy decreases to derive the relative activities of the ions of the base and its activity coefficients at various concentrations (compare MacInnes and Parker, A., 1915, ii, 510, on the free energy of potassium chloride, and Ellis, A., 1916, ii, 369, and Noyes and Ellis, A., 1918, ii, 27, on hydrochloric acid). The cells studied were of the type $Hg + HgO - KOH(c_1) - K$ in $Hg - KOH(c_2) - Hg + HgO$ at 25°. The potassium amalgam was used in the form of a dropping electrode, and potassium hydroxide concentrations were varied between 0·003 and 0·84N. As found by Ellis in the case of hydrochloric acid, the activity coefficient at first decreases with increasing concentration. It passes through a minimum at about 0·5 molal concentration, then increases rapidly. Up to concentrations of 0·5 molal, the activity coefficient has a much smaller value than the conductance-viscosity ratio, showing that this ratio, even at moderate concentrations, is not even an approximate measure of the effective ionisation of highly ionised substances. E. H. R.

The Activities of the Ions in Solutions of Mixed Electrolytes. MING CHOW (*J. Amer. Chem. Soc.*, 1920, **42**, 497—502).—Determinations of the activity coefficients in mixed solutions of hydrochloric acid and potassium chloride were made from measurements of the electromotive force of cells of the type $H_2(1\text{ atm.}) - HCl(c_1) + KCl(c_2) - Hg_2Cl_2 + Hg$, in which the separate concentrations c_1 and c_2 were varied, but their sum was kept constant at 0·1N. The results show that the activity

coefficient of the hydrochloric acid has substantially the same value in all the mixtures, and lend support to the view that the activity of the chlorine ion in solutions of different highly ionised univalent chlorides or of mixtures of them is determined by its own concentration, and is independent of the cations associated with it. The experimental results do not agree with those obtained by Loomis, Essex, and Meacham (A., 1917, ii, 353) from *E.M.F.* measurements of the same type of cell. E. H. R.

The Theory of Electrolytic Ions. XIII. Conductivity of Multivalent Electrolytes. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, **109**, 63—68. Compare A., 1919, ii, 262).—A correction and extension of the theoretical conceptions, on the step-wise ionisation and the degree of dissociation, put forward previously (*loc. cit.*). J. F. S.

The Phenomena of Electrolytic Migration. Electrolysis of Mixed Solutions of Alkali Salts. MARC H. VAN LAER (*Rec. trav. chim.*, 1920, **39**, 301—329).—In the electrolysis of a normal solution of sodium hydroxide at 18°, the yield from the current is only 17·5% of that indicated by Faraday's law, but this yield is often varied by the superposition of different factors; thus, according to the direction in which they act, the hydrostatic pressure, diffusion, and electrical osmosis may favour the migration of certain ions and retard that of the ions of opposite sign. Other intervening factors are temperature, the intensity of the current, and the nature of the diaphragm between the anode and cathode liquids. Thus, in the electrolysis of a solution of sodium hydroxide, rise in temperature and cataphoresis both exert a favourable influence. On the other hand, the diffusion of the sodium hydroxide produces a loss, which increases with the concentration of the cathode liquid. As the concentration of the current, I/V, diminishes, the yield first increases gradually until it reaches a maximum and then decreases.

The electrolysis of a solution of sodium carbonate presents the same fundamental characteristics as in the case of sodium hydroxide, but in this case, as the electrolysis proceeds, the resistance of the cell increases, owing to the formation of sodium hydrogen carbonate, the carbon dioxide liberated at the anode being entirely absorbed by the solution at the ordinary temperature if the current intensity is not too great. The introduction into the solution of an oxy-salt, such as the sulphate, chlorate, or nitrate of sodium with a common cation, prevents the formation of sodium hydrogen carbonate, and thus a cathode liquid very rich in sodium hydroxide can be obtained. The nitrate gives the best result, and the yield from the current increases with the concentration of the oxy-salt.

Applying this method to barium carbonate in the presence of barium nitrate, the solid carbonate being introduced into the anode vessel, crystalline barium hydroxide was readily obtained. W. G.

Diamagnetism of Odorous Substances. H. ZWAARDEMAKER and F. HOGEWIND (*Arch. Néerland. Physiol.*, 1920, **4**, 224—232).—The authors have measured the diamagnetism of a large number of odorous substances, and plotting the values found against the number of atoms in the molecule, it is found that, for an homologous series, the points lie on practically a straight line, but that the differences between the values obtained for adjacent members in a series vary from series to series. W. G.

A Method for Determining the Relationship between the Melting Point of a Crystal Lamella and its Thickness. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **110**, 166—168).—The method suggested is to form by crystallisation a lamella of variable thickness between a plate and a cylindrical lens, and to have in the metal plate a temperature gradient so that the contact line between the plate and the lens is perpendicular to the isotherms in the plate. If the melting point lies between the temperatures of the two ends of the plate, part of the substance melts, and the bounding curve between the liquid and crystalline portions shows by its form the influence of the thickness of the lamella on the melting point. The work required to disrupt the crystal is inversely proportional to the thickness of the lamella, and it follows that the influence of the lamella thickness on the melting point is also inversely proportional to the lamella thickness. Thermodynamically, it is shown that the work required is equal to the change of equilibrium temperature multiplied by the entropy of unit mass at the melting point. E. H. R.

The Influence of State of Division on Melting Point. F. MEISSNER (*Zeitsch. anorg. Chem.*, 1920, **110**, 169—186).—The conclusions of Pavlov (A., 1909, ii, 19, 295, 800; 1910, i, 740) regarding the influence of size of particles on melting point are adversely criticised. The growth of large crystals at the expense of small ones is to be attributed, not to difference of vapour pressure between large and small crystals, but to fluctuations in temperature. Pavlov's observation that small particles of salol, 8 to 15 μ in diameter, melt several degrees below the normal melting point, could not be confirmed.

The only satisfactory method of examining the relation between state of division and melting point is by the investigation of thin lamellæ, formed by allowing a molten substance to crystallise between two plates. Such lamellæ admit of theoretical treatment, in which the surface energy of the crystal can be considered in the same manner as that of a liquid. If $A_0 - A'_0$ be the difference between the surface energies of crystal and liquid, the following relation holds: $A_0 - A'_0 = (T_1 - T_2)/T_0 . RQ/2 . d_1d_2/(d_1 - d_2)$, where T_0 is the normal melting point, T_1 and T_2 the fusion temperatures of lamellæ of thickness d_1 and d_2 respectively, R the latent heat of fusion, and Q the density of the fused substance. To determine the value of $A_0 - A'_0$, it is necessary to know the relation between melting point and lamella thickness. The experimental method

used was that suggested by Tammann (preceding abstract), in which wedge-shaped lamellæ were formed between a cylindrical lens and a metal plate having a uniform temperature gradient from end to end. In the cases of azobenzene, tristearin, and myristic acid, the boundary curves formed between solid and liquid were distinctly displaced towards the cold end of the plate as the thickness of the lamella diminished. In the case of azobenzene, the displacement represented a difference of 0·355° in the melting point for a change of thickness from 0·8 to 10 μ. In the case of tristearin, the temperature difference was 0·199°, and for myristic acid 0·258°. The surface energy differences between crystal and liquid, calculated from the above equation, were in the three cases 67, 50, and 59 ergs respectively. In a number of other cases, including salol, acetamide, and glauber salt, the temperature difference was of the same order as in the case of myristic acid, whilst with *p*-chloroaniline and stearic acid, no difference due to diminishing thickness of the lamella could be detected.

E. H. R.

Phenomena Observed during the Melting, Freezing, and Boiling of Mixtures of Ammonium Chloride and other Chlorides. KURT HACHMEISTER (*Zeitsch. anorg. Chem.*, 1919, 109, 145—186).—Cooling curves have been constructed for ammonium chloride, cuprous chloride, lithium chloride, zinc chloride, cadmium chloride, ferric chloride, thallous chloride, and lead chloride, and for mixtures of ammonium chloride with cuprous chloride, lithium chloride, zinc chloride, cadmium chloride, ferric chloride, thallous chloride, and lead chloride. Very complete diagrams of condition are constructed for the binary mixtures. In connexion with the simple salts, much of the data obtained differs from that previously published. The transition point of ammonium chloride is found to be 174° (Wegscheider, A., 1918, ii, 298, 184·5°). The following melting points are obtained: cuprous chloride, 425°; lithium chloride, 605°; zinc chloride, 283°; cadmium chloride, 568° (b. p. 964°); ferric chloride, 303°; thallous chloride, 427°; lead chloride, 501°. It is shown that by mixing other chlorides with ammonium chloride, this substance may be obtained molten. The compounds $CdCl_2,NH_4Cl$, $2ZnCl_2,NH_4Cl$, and $FeCl_3,NH_4Cl$, in addition to the double compounds already known, are indicated by the temperature composition diagrams. In the binary mixtures of ammonium chloride with cuprous chloride and lithium chloride, respectively, simple eutectics are formed, but no compounds. The compound formed between equimolecular quantities of ferric chloride and ammonium chloride is peculiar in possessing a definite boiling point, 386°. Mixtures of ammonium chloride with lead chloride and thallous chloride, respectively, cannot be melted. Ammonium chloride shows great similarity in its behaviour with other chlorides to the alkali chlorides. The nearer the two chlorides are in general properties, the simpler is the binary system formed between them.

J. F. S.

Melting Points of the Members of Homologous Series. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1919, **109**, 221—225).—A theoretical paper in which regular rise and fall of the melting point of members of the monocarboxylic aliphatic acids is discussed. It is suggested that the acids with an even number of carbon atoms exist in two stable, crystalline forms, and that this furnishes the reason for the course of the melting points in this series. In support of this hypothesis, it is shown that acetic acid exists in two such forms, the triple point of which lies at 57·5° under a pressure of 2330 kilos. per sq. cm. No such isomerides have been observed for the acid with an uneven number of carbon atoms, formic acid. J. F. S.

Critical Data and Chemical Constitution. W. HERZ (*Zeitsch. anorg. Chem.*, 1919, **109**, 293—296).—A theoretical paper in which the author has tabulated the critical pressure and critical temperature of a large number of members of the following homologous series: paraffins (9), olefines (3), methyl esters of the monocarboxylic aliphatic acids (6), ethyl esters of the same acids (6), ethers, amines (6), benzene hydrocarbons (11), aromatic amines (3), and other organic substances. It is shown that the critical temperature increases with increasing number of carbon atoms, and the critical pressure decreases with increasing number of carbon atoms. When the quotient of the critical temperature in absolute degrees and the critical pressure is divided by the number of carbon atoms, an approximate constant is obtained (2·5—4·0) for aliphatic compounds and 1·9—2·4 for aromatic compounds. A much better constant is obtained if, instead of the number of carbon atoms, the total number of atoms is used; here the constant is 0·99—0·69 for aliphatic compounds and 0·98—0·90 for aromatic compounds. Further, if the quotient is divided by the total number of valencies, a very good constant is obtained, 0·50—0·41 for aliphatic compounds and 0·43—0·37 for aromatic compounds. J. F. S.

New Instrument for Measuring Vapour Tension. HAROLD MOORE (*J. Soc. Chem. Ind.*, 1920, **39**, 78—80T).—An instrument for making rapid and accurate measurements of the vapour pressure of motor spirit is described. It consists of two tubes about $\frac{1}{4}$ in. bore and 800 mm. long connected to each other and to a levelling bottle by means of a Y-piece and thick-walled rubber tubing. The two tubes are clamped vertically, and have mercury-sealed cocks at their upper ends, which close the tubes to small, graduated cups. One of the tubes is surrounded by a water-jacket. To make a measurement, the whole apparatus is filled with mercury, then a measured volume of spirit is admitted into one of the tubes from the small cup at the top, and the reservoir lowered. The barometric height is read from one tube, and the barometric pressure diminished by the vapour pressure of the spirit is read from the other tube. The vapour pressure of crystallisable benzene, ethyl alcohol, and petrol has been deter-

mined over the temperature range 10—50°, and also the vapour pressure of a series of mixtures of alcohol and petrol and alcohol and benzene at 20°, 30°, 40°, and 50°. Working with water, the error observed in the vapour pressure was about 3 mm., but with mixed motor spirits it will probably be much greater. J. F. S.

The Vapour Pressures of Cadmium, Lead, and Tin Amalgams. JOEL H. HILDEBRAND, A. H. FOSTER, and C. W. BEEBE (*J. Amer. Chem. Soc.*, 1920, **42**, 545—548).—A continuation of previous work on the vapour pressures of liquid amalgams (compare A., 1913, ii, 471, 755; 1914, ii, 800; 1916, ii, 14). The vapour pressures of mercury over amalgams of cadmium, lead, and tin were measured at 324°, by the method previously described, at intervals covering the entire range of concentrations, and the values of the constants a and c were calculated in the empirical equation $\log p/p_0 = \log N + a/(1+cn)^2$, where n represents the number of molecules of mercury per molecule of the other metal, $N = n/n+1$, p_0 is the vapour pressure of pure mercury, and p that of the amalgam of composition corresponding with n. Cadmium amalgams show vapour pressures less than those demanded by Raoult's law, $p/p_0 = N$, and the deviations can be calculated on the assumption of partial solvation, varying with the concentration according to the mass law, to form molecules of CdHg. Lead and tin amalgams give practically equal vapour pressures, which are much greater than Raoult's law demands. The deviations cannot be accounted for by the assumption of any simple molecular change. E. H. R.

The Aqueous Pressure of some Hydrated Crystals. Oxalic Acid, Strontium Chloride, and Sodium Sulphate. GREGORY PAUL BAXTER and JOHN ERNEST LANSING (*J. Amer. Chem. Soc.*, 1920, **42**, 419—426).—With the object of perfecting a trustworthy method of measuring the aqueous pressures of hydrated crystals, experiments were made with oxalic acid, strontium chloride, and sodium sulphate, and the following method was found to give satisfactory results. The hydrated crystals were intimately mixed with 5—10% by weight of the dehydrated substance, and the mixture was packed, interspersed with glass beads, in a large U-tube. The method of experiment was to pass a measured volume of dry air through the column of crystals at constant temperature, subsequently passing the air through weighed drying tubes containing phosphoric oxide. The curves obtained by plotting the logarithm of the vapour pressure found against the reciprocal of the absolute temperature were very nearly straight lines, almost exactly so in the case of sodium sulphate crystals. E. H. R.

The Vapour Pressures of Concentrated Solutions. G. R. PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 59—72).—Measurements were made between 0° and 40° of the vapour pressures of solu-

tions of (1) potassium hydroxide for concentrations between 18·81 and 138·2 grams of the anhydrous hydroxide in 100 grams of water; (2) sodium hydroxide for concentrations between 14·62 and 113·1 grams in 100 grams of water; (3) calcium chloride for concentrations between 14·81 and 119·5 grams of the anhydrous salt in 100 grams of water. The results obtained for potassium hydroxide are not in very close agreement with those obtained by Dieterici (compare A., 1891, 783; 1898, ii, 207; 1899, ii, 403).

W. G.

Determination of Boiling Point. SCHIMMEL & Co. (*Bericht.* April-October, 1919, 100—102; from *Chem. Zentr.*, 1920, ii, 422—423).—In connexion with the apparatus described recently by Paul and Schautz (A., 1919, ii, 422), the authors recommend the adoption of definite normal pressures for data concerning boiling points, particularly for such as are determined in a vacuum. As absolute unit of pressure, the bar (one dyne per sq. cm.) is advocated. One atmosphere = 1,013,200 bars, or 10 kilobars correspond fairly closely with 75 mm. Measurements should be effected at normal pressures, a simple type of apparatus for the measurement of the latter being depicted in the original. Measurement of pressure in vacuum distillation (particularly in a high vacuum) is only accurate when it is effected close to the point at which the temperature is observed. The errors in the older method, in which the manometer is attached to the exhaust pipe, increase with increase of the vacuum and the velocity of distillation, with the decreasing width of distillation and condensing tubes, and with leaks in the apparatus.

H. W.

Physical Behaviour of Liquids. W. HERZ (*Zeitsch. Elektrochem.*, 1920, **26**, 109—111).—A theoretical paper in which formulæ are developed whereby the molecular boiling-point elevation and the capillarity constant at the boiling point may be calculated from the critical data. These formulæ have the form: (1) $c = 4T_k^2 d_k/3p_k$; (2) $a = 0·03643p_k/d_k$, in which p_k is the critical pressure, T_k the critical temperature, d_k the critical density, c is the molecular elevation constant, and a the Poisson capillarity constant. A further formula for calculating the vapour pressure is also developed; this has the form

$$\log(p_s/p_1) = 4·91(T_s/T_1 - 1),$$

in which p_s is the vapour pressure at the boiling point T_s, and p_1 the vapour pressure at the temperature T_1. The values obtained by the use of these formulæ have been compared with the experimental values, and found in the case of non-associated liquids, both organic and inorganic, to be in good agreement.

J. F. S.

Vapour Tension and Heat of Vaporisation, and the Dependence of the Factors a and b on the Temperature and the Volume. J. J. VAN LAAR (*Rec. trav. chim.*, 1920, **39**, 215—242).—A mathematical discussion of the subject. W. G.

A Thermodynamic Investigation of Reactions Involving Silver Sulphide and Silver Iodide. ARTHUR A. NOYES and E. STANLEY FREED (*J. Amer. Chem. Soc.*, 1920, **42**, 476—487).—The equilibrium at 25° of the reaction

$$Ag_2S(\text{solid}) + 2H^+I^-(\text{in water}) = 2AgI(\text{solid}) + H_2S(\text{in water})$$

was studied with the object of determining how the activity coefficient (or effective ionisation) of the acid varies with its concentration, and to determine the free energy change attending the reaction. The concentration of hydriodic acid was necessarily confined within the limits 0·024 to 0·116*N*. The equilibrium constant, *K*, calculated from the formula $K = C_{H_2S}/(C_{HI}\gamma)^4$, where γ is the ionisation constant, has a mean value 964. Assuming that the activity coefficient at $C_{HI}=0·025N$ is identical with the ionisation constant, it is found that between concentrations 0·025 and 0·12 the activity coefficient decreases 4·5%, compared with 8·3, found by Noyes and Ellis for hydrochloric acid (A., 1918, ii, 27).

E.M.F. measurements were made between 5° and 25° of the cells

$$H_2(1\text{ atm.}) - HCl(0·5—0·1N) - \{HCl(0·5—0·1N), H_2S(1\text{ atm.})\} - Ag_2S + Ag,$$

and at 25° of the cells

$$H_2(1\text{ atm.}) - HI(0·30—0·98N) - AgI + Ag.$$

From the data obtained, a number of free energy calculations are made, and are compared with the results of calculations made using data from other sources. Finally, the following figures are adopted: for the free-energy decrease attending the reaction $2AgI + H_2(1\text{ atm.}) = 2Ag + 2H^+ + 2I^-$ at 25°, −6885 cal., and for the reaction $Ag_2S + H_2(1\text{ atm.}) = 2Ag + H_2S(1\text{ atm.})$ at 25°, −1485 cal. Making use of the value found for the free energy of formation of iodide ion by Lewis and Randall (A., 1914, ii, 840), the free-energy value for the reaction $2Ag + I_2 = 2AgI$ is found to be +31,493 cal. Half this quantity is the free-energy decrease attending the formation of one molecule of solid silver iodide from its elements at 25°. E. H. R.

Use of Lead Electrodes for Thermochemical Measurements. CONSTANZE KRAHMER (*Zeitsch. Elektrochem.*, 1920, **26**, 97—104).—The *E.M.F.* of cells of the type

$$Pb\,|\,PbCl_2(\text{sat.})\,\|\,Hg_2Cl_2\,|\,Hg,$$

$$Pb\,|\,PbCl_2(\text{sat.})\,\|\,AgCl\,|\,Ag,\ Pb\,|\,PbBr_2(\text{sat.})\,\|\,AgBr\,|\,Ag, \text{ and}$$

$$Pb\,|\,PbI_2(\text{sat.})\,\|\,AgI\,|\,Ag$$

has been measured at a number of temperatures, and from the data thus obtained the heat of formation of lead chloride, silver bromide, and silver iodide has been calculated. The lead electrodes were prepared on platinum wire by electrolysing a solution of 8% hydrofluosilic acid and 4% lead silicofluoride by means of a current of 0·001 ampere. The *E.M.F.* of the cell

$$Pb\,|\,PbCl_2(\text{sat.})\,\|\,Hg_2Cl_2\,|\,Hg$$

is given by the formula $E_{293} = 0·53113 - 0·000191(20 - t)$, and the

heat of the reaction $\frac{1}{2}Pb + HgCl = \frac{1}{2}PbCl_2 + Hg$ is $U_{293} = 10{,}949 \pm 0.1\%$ cal., from which the heat of formation of lead chloride is calculated to 85,521 cal. In the case of the cell

$$Pb \mid PbCl_2(sat.) \parallel AgCl \mid Ag,$$

$E_{293} = 0.49328 + 0.000125(t - 20)$, $U_{293} = 12{,}211 \pm 24$ cal., and assuming the heat of formation of silver chloride to be 30,505 cal., the heat of formation of lead chloride is 85,432 cal. The *E.M.F.* of the cell $Pb \mid PbBr_2(sat.) \parallel AgBr \mid Ag$ is

$$E_{293} = 0.35252 + 0.000126(20 - t^\circ)$$

and $U_{293} = 8974 \pm 44$ cal.; using the value 66,350 cal. for the heat of formation of lead bromide, the heat of formation of silver bromide is found to be 24,201 cal. In the case of the cell

$$Pb \mid PbI_2(sat.) \parallel AgI \mid Ag,$$

$E_{293} = 0.21205 + 0.000129(20 - t)$ and $U_{293} = 5758 \pm 57$ cal., and the heat of formation of silver iodide is 15,192 cal. When the haloids used were crystalline, slightly different values are found for the above-named cells. A number of experiments with evacuated elements show that the gradual falling of the *E.M.F.* of the cell $Pb \mid PbCl_2(sat.) \parallel Hg_2Cl_2 \mid Hg$ is not due to oxidation, but is in some way connected with the size of the lead crystals. A table of comparison of the present values with those of Thomsen, Berthelot, and other observers is included in the paper. J. F. S.

Heat of Solution. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **109**, 215—220).—A theoretical paper in which it is shown that from a knowledge of the heat of solution of one substance in another, it is possible to decide whether or no a chemical reaction has taken place during solution. The heat of solution is made up of heat quantities brought about by (i) the conversion of an anisotropic substance into an isotropic condition, (ii) the mixture of the isotropic substance with the solvent, and (iii) chemical processes, such as formation of compounds, change in molecular weight, and ionisations. The dimensions of the first two quantities can be calculated theoretically, hence from the experimentally determined heat of solution it is possible to see whether any heat change due to the third cause is contained in the experimental value, and so ascertain whether chemical processes have taken place. J. F. S.

Heat of Solution and the Partial Molal Heat Content of the Constituents in Aqueous Solutions of Sodium Chloride. MERLE RANDALL and CHARLES S. BISSON (*J. Amer. Chem. Soc.*, 1920, **42**, 347—367).—The partial molal heat content of a substance is its heat content when in solution at a given concentration, and is defined as the increase in the heat content of a large amount of the solution at the given concentration when one mol. of the substance is added to it. The symbol $\bar{H}$ is used for this quantity, and H for the absolute molal heat content of the substance. It follows that the partial molal heat of solution of a substance, for example, sodium chloride, is given by $\bar{H}_c - H_{NaCl}$

for a concentration c. The symbol ΔH is used to represent the partial molal heat content of a substance formed from its elements in their standard state at the same temperature. The specific heats of sodium chloride and potassium chloride solutions were first determined for different concentrations at 25°. The partial molal heat of solution of water in sodium chloride solution, $\bar{H}-H_{H_2O}$, was determined by measuring the heat absorbed per mol. of water when water was added to sodium chloride solutions of known concentrations. Starting with saturated sodium chloride solutions, the values rise gradually from about 11 cal. at $6{\cdot}25M$ to 21 cal. at $4{\cdot}2M$, and then gradually diminish to zero at infinite dilution.

The heat of dilution of sodium chloride was also measured calorimetrically by adding small amounts of saturated solution to a large volume of water. The value found at infinite dilution was 606 cal. The mean heat of solution of sodium chloride in a very large amount of water was found experimentally to be 1019 cal. From the values obtained, the partial molal heat content of sodium chloride, ΔH, at 25° in solution at all concentrations was calculated. The value of ΔH increases from $-96{,}781$ at infinite dilution to $-97{,}500$ in a saturated solution, whilst the partial molal heat content of the water decreases from $-68{,}272$ at infinite dilution to $-68{,}250$ at $4{\cdot}2M$, increasing again to $-68{,}261$ in a saturated solution. E. H. R.

Chemical Affinity. XII. Thermodynamical Relationship between the Mixture Affinities of Partially Saturated Solutions and its Application to the Estimation of Affinity. J. N. Brönsted (*K. Danske. Vidensk. Medd. Math. Phys.*, 1918, 1, No. 5, 1—39; from *Chem. Zentr.*, 1920, i, 404—405. Compare this vol., ii, 298).—A relationship has been established between the mixture potentials of two components in a mixture in which the potential of the other substances present is maintained constant, as, for example, by invariably using solutions saturated with these substances. The relationship may be expressed by the equation $x.dA_1/d_x+(1-x)dA_2/dx=0$ or $n_1dA_1+n_2dA_2=0$, in which A_1 and A_2 are the molecular differential mixture potentials of the components, and n_1 and n_2 the number of molecules in the mixture. The equation has therefore the same form as if the two components are present in binary mixtures. The theory is developed for the formation of double salts, for allotropic transformation, and for reciprocal pairs of salts, and is applied in particular to the cases of α- and β-$CaCl_2,4H_2O$ and of carnallite and schönite. The affinity of the reactions $KCl+NaClO_3 \longrightarrow KClO_3+NaCl$ and $KCl+NaNO_3 \longrightarrow KNO_3+NaCl$ has been measured at 16·39° by estimation of the vapour pressure; the values 2020 cal. and 740 cal. are obtained, which agree closely with the data previously deduced from electrometric measurements, and thus afford a sharp verification of the theory. An experimental method is also described which permits the simultaneous estimation of

vapour tension and concentration of solutions, and also indicates in a simple manner the points at which saturation in respect to one or two components occurs. H. W.

A Surface Tensimeter for Small Quantities of Liquids. C. C. KIPLINGER (*J. Amer. Chem. Soc.*, 1920, **42**, 472—476).—A method has been devised by means of which the surface tension of a liquid may be determined when only a drop or two is available. A capillary glass tube, about 18 cm. long, 1 mm. internal and 4 mm. external diameter, is carefully made with its ends, as nearly as possible, plane and accurately rectangular with the length. By means of a special device (A., 1918, ii, 360), the tube can be attached to a quadrant cut from a celluloid protractor. A small notch cut in the apex of the quadrant holds in position a thread, which passes over it, the thread carrying a small weight at each end and serving to indicate the angular displacement of the tube. The apparatus is held in position by a suitable clamp on a stand. A short column of the liquid to be examined is introduced into the clean, dry capillary tube, and the tube is turned through such an angle that the meniscus at the lower end changes to a plane surface. The point at which this occurs is observed by means of a pocket lens, and the angular displacement from the vertical is read off on the quadrant. The length, l, of the column is measured to 0·1 mm., and from the equation $l \cos A = h$, the height, h, of the vertical column exerting the same pressure as the inclined column of liquid is calculated. The surface tension is then calculated from the usual formula, $T = d \times h \times r \times 980/2$ dynes per cm. The results obtained are generally 2—4% low. The method may be used to assist in identifying organic liquids. E. H. R.

Adsorptive Power of Different Forms of Charcoal. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 348—350).—The most adsorptive charcoal was obtained by heating the material to be charred to a high temperature. Low-temperature carbonisation of filter paper, or previous impregnation of the material with sodium chloride, gave an inferior adsorbent. W. S. M.

Some Aspects of the Behaviour of Charcoal with respect to Chlorine. G. S. BOHART and E. Q. ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 523—544).—Experiments on the absorption of chlorine by charcoal showed considerable variations in the behaviour of single samples, which could only be attributed to differences in the humidity of the current of chlorine-laden gas. A series of experiments was therefore carried out on the effect of moisture and, in addition, the influence of variations in temperature and pressure, of the velocity of the gas through the charcoal and of the density of the charcoal and the depth of the absorbing layer, were studied. Two processes take place during the passage of the gas through the charcoal, absorption or adsorption, which cannot be distinguished, and catalytic formation of hydrochloric acid. The results of the

experiments are illustrated by means of curves, in which the percentage of chlorine or hydrochloric acid transmitted is plotted against time. The period during which no chlorine or hydrochloric acid is transmitted is called the service time of the charcoal. The service times of different charcoals could not be correlated with their apparent density. For any one sample of charcoal, the service time increases more rapidly than the thickness of the absorbing layer. Charcoals with the greatest chlorine capacity were found to be the best catalysts for the reaction between water and chlorine. The effect of humidity was studied by varying the moisture content of the gas stream, air to chlorine in the ratio 500:1, from 0—80% saturation at 25°. Hydrogen chloride always appeared in the transmitted gases before chlorine, and when chlorine appeared as well, the effect of the moisture could be seen, particularly in the 80% saturation experiment, in the greater proportion of acid to free chlorine. The duration of complete chlorine absorption passes through a minimum at about 50% saturation. Below 12·5°, chlorine appeared in the gases before hydrogen chloride; above this temperature, the reverse was the case. The service time is at a minimum between 0° and 12·5°. Reductions in pressure have little, if any, effect. The chlorine capacity of the charcoal is increased by one exposure to chlorine, followed by heating to dull redness in a vacuum. E. H. R.

The Velocity of Adsorption of Chloropicrin and Carbon Tetrachloride by Charcoal. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1920, **42**, 372—391).—The experiments recorded were carried out for the purpose, first, of obtaining reproducible results in the measurements of the velocity of adsorption of gases on a relatively gas-free solid surface, and, secondly, of determining the effect of a foreign gas on this velocity. The method of experiment adopted was to expose the charcoal for a measured time to the vapour to be adsorbed at a low pressure (the vapour pressure of the compound), and to determine the amount of adsorption by the increase in weight of the charcoal. Charcoal was chosen for examination on account of its exceedingly large adsorbing surface, and chloropicrin and carbon tetrachloride as gases on account of their relatively high molecular weight, and the consequently relatively considerable weight of gas adsorbed. The results are shown by series of curves, in which the weight of gas adsorbed per gram of charcoal is plotted against time. In no case could reproducible results be obtained until the charcoal had been heated to more than 700° in a vacuum, cooled in a vacuum, exposed to the gas until a considerable quantity was adsorbed, and again heated above 700° in a high vacuum. This process of washing out with the gas under examination is necessary to remove foreign gases, which cause an initial lag in the adsorption. When the charcoal is in such a condition that the maximum velocity of adsorption is attained, the process follows the equation

$$m = 1/t \, . \log A/A - K,$$

where K is the amount adsorbed per gram of charcoal in time t and A is the amount adsorbed when t is infinite, m being a constant. The curve obtained by plotting $\log A/A-K$ against t is then a straight line. The results are in agreement with Langmuir's theory of adsorption (A., 1918, ii, 430), in which he assumes that the adsorbed layer of gas is only one molecule deep. Some of the results for carbon tetrachloride indicate the possibility of the formation to a certain extent of a second adsorbed layer, but the influence of small quantities of foreign gases on the rate of adsorption may account for the divergence of the curves, in these cases, from straight lines.

E. H. R.

Evaluation of Dissociation Measurements of [Metal] Ammines by means of the Nernst Theorem and Nomograms. WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1919, **109**, 111—125. Compare this vol., ii, 318).—A theoretical paper in which the method of evaluating and comparing dissociation pressures of ammines is described. The heat of dissociation at the absolute zero (Q_0) and the coefficient of T are determined from the Nernst equation $\log p = -Q_0/4\cdot57T + 1\cdot75 \log T + (\Sigma\nu\beta + \Sigma nb)/4\cdot57 . T + 3\cdot3$. Nomograms are given by means of which the calculations, both for the complete and the approximate Nernst formula, are replaced by readings from scales. The value of Q_0 is shown to be constant in the case of the ammines of iron, cobalt, nickel, and manganese, and is in agreement with the calorimetric values and those calculated according to the van't Hoff rule. The coefficient of T is, within the limits of experimental error, in keeping with the thermochemical data; it is independent of the nature of the ammonia-free salt, but depends on the nature of the linking of the combined ammonia. The combined ammonia has a larger molecular heat in the hexammines than in those compounds with less ammonia. The dissociation temperature of all the ammines is determined by the nomograph for $p=100$ mm. The values are compared with those obtained by a graphic approximation method, and the two sets of values shown to be in moderate agreement. The nomographic method is superior to the graphic method, and also more convenient in use.

J. F. S.

Nomographs from the Functions Log $p = -Q/4\cdot57T + 1\cdot75$ Log $T + C$ and Log $p = -Q/4\cdot57T + 1\cdot75$ Log $T - aT + 3\cdot3$. H. VON SANDEN (*Zeitsch. anorg. Chem.*, 1919, **109**, 126—131. Compare preceding abstract).—A theoretical paper in which the method of drawing and using nomographs is described. A nomograph is a series of lines and curves by which the relationships of functions with several variables may be represented (see "Traite de Nomographie," d'Ocagne). In the case of the two functions named above, the nomograph is constructed as follows. Two vertical lines are drawn, of which the one standing to the left is graduated for pressure in millimetres of mercury; the other is divided to

give values of Q; to the right of these lines, a series of curves are drawn, one for each value of C or a, and each of these curves is subdivided to give temperature values. To illustrate the use of the nomograph thus constructed, an example will best serve. Suppose Q, T, and C are known and the corresponding value of p is desired. The value of T on the appropriate C curve is sought out, and the point joined by a straight line with the corresponding Q value. The line is then produced, and the point where it cuts the pressure line gives the corresponding p value. J. F. S.

Diffusion of Organic Substances in Organic Solvents and the Examination of Stokes' Formula. ERNST DUMMER (*Zeitsch. anorg. Chem.*, 1920, **109**, 31—51).—The author has determined the diffusion coefficient, the viscosity, and index of refraction of nitromethane, ethyl acetate, nitrobenzene, benzotrichloride, acetone, ethyl benzoate, and methyl alcohol, and solutions of these substances in one another. From the results, the radius of the various molecules is calculated by means of the Stokes-Einstein formula $D=RT/N.1/6\pi rk$, in which $R=8{\cdot}32\times10^7$ and $N=6{\cdot}20\times10^{23}$, and these values are compared with the theoretical values. It is shown that the radius in a given case is different, depending on the molecular weight of the diffusing substance and the solvent. Certain regularities are apparent in the results; thus a smaller value is found for the radius of a given substance the larger the molecular weight of the solvent. An exception to this is found only in the calculation of the radius from the diffusion of ethyl benzoate into methyl alcohol, and from the diffusion of nitrobenzene into methyl alcohol. From the results, it can be stated generally that the Stokes-Einstein formula may only be applied to the region of molecular dimensions with the greatest caution. J. F. S.

Solubility. I. Solubility of Salts in Solutions of Salts. J. N. BRÖNSTED (*K. Danske. Vidensk. Medd. Math. Phys.*, 1919, **2**, No. 10. 1—46; from *Chem. Zentr.*, 1920, i, 402—403).—The theory of the solubility of salts in solutions of salts is developed on the preliminary hypothesis that the coefficient of activity in a mixed salt solution is the same for every ion of the same type. The calculation of the coefficient of activity, f, is based on the observation of Noyes and Falk that the behaviour of a number of binary salts can be summarised by the expression $2-i=K\sqrt[3]{c}$ in which i is van't Hoff's factor, c the equivalent concentration, and K a constant which is characteristic for each salt; by the substitution of $2a=K$, the following equation is derived: $\log^{10}f=-1{\cdot}373a\sqrt[3]{c}=-a\sqrt[3]{c}$. The development of the theory depends on whether the solvent and dissolved substance have a common ion or not; both cases are considered and illustrated by experimental data. The following solubilities are cited: dichlorotetramminecobalt thiocyanate in sodium chlorate solution; *trans*-dinitrotetramminecobalt in potassium formate solution; oxalo

tetramminecobalt perchlorate in sodium formate solution; dichlorotetramminecobalt bromide in potassium bromide solution; *trans*-dinitrotetramminecobalt chloride in potassium chloride solution; *iso*thiocyanopentamminecobalt sulphate in magnesium sulphate solution. H. W.

Supersaturation and Crystal Size. Wilder D. Bancroft (*J. Physical Chem.*, 1920, **24**, 100—107).—A theoretical paper in which the theory put forward by von Weimarn in connexion with the relationship between the degree of supersaturation and the size of crystals ("Grundzüge der Dispersoidchemie," 1911, 39) is discussed and shown to be inadequate, because it does not take account of the number of nuclei formed. It is shown that, with vigorous stirring and increasing supersaturation, a substance, which normally is precipitated anhydrous, may be obtained as a colloidal solution, a curdy precipitate, fine crystals, coarse crystals, or a gelatinous precipitate. At higher temperatures, precipitates are, as a rule, more coarsely crystalline than at lower temperatures. The theory of von Weimarn applies to solutions which are not stirred. The conditions for forming large crystals are those in which there is no spontaneous formation of nuclei and in which the rate of crystallisation is so slow that branched crystals do not form. The effect of adsorption on the growth of crystals is not adequately covered by von Weimarn's theory. J. F. S.

The Relation between Growth Forms and the Structure of Crystals. Paul Niggli (*Zeitsch. anorg. Chem.*, 1920, **110**, 55—80).—A theoretical paper in which the modern theory of crystal structure is applied to the discussion of the development of crystal forms both during the growth of a crystal and during its dissolution. The faces which attain maximum development are perpendicular to the directions of maximum velocity of growth, and these faces correspond with the principal planes in the lattice structure. The whole crystal is regarded as a polymerised co-ordinated compound; the inner atoms are saturated, but those on the surface are unsaturated in certain directions. It is shown that, since the directions in which the unsaturated valencies are active are determined by the structure of the crystal, faces with complex indices should grow with greater velocity than simpler faces, because the development of such complex faces exposes to a greater extent the free atomic valencies. To a certain depth, which can be calculated, the crystal can be regarded as imperfectly formed in the plane of these complex faces, and the greater the depth of this partly crystalline layer, the greater will be the velocity of growth of the corresponding face. Statistical calculations for different types of cubic crystals show that the theoretically most probable faces are those which indeed actually occur, for example, in crystals of sodium chloride and zinc blende. The occurrence of vicinal faces is also in accordance with the theory. E. H. R.

Structure Distortion in Plastic Fluid Crystals. O. LEHMANN (*Ann. Physik*, 1920, [iv], **61**, 501—532).—An account of some experiments on the optical properties of fluid crystals. Mixed fluid crystals, for example, cholesteryl chloride and propionate, when mechanically distorted between a microscope slide and cover slip, exhibit optical rotation, varying in magnitude and direction with the proportions of the two constituents present. E. H. R.

Electrical Double Refraction of Colloids. C. BERGHOLM and Y. BJÖRNSTÅHL (*Physikal. Zeitsch.*, 1920, **21**, 137—141).—Sols of vanadium pentoxide, gold, and silver have been examined, by means of a method employed by Brace (*Phil. Mag.*, 1904, [vi], **7**, 317), under the influence of an alternating electric field, and in every case shown to be double refracting. This implies that the particles of these sols are not spherical and do not possess spherical symmetry. The double refraction in a gold sol, the particles of which have a diameter of about 100 $\mu\mu$, changes with the frequency; with a potential of 400 volts per cm., the phase difference is 35% greater at 3000 periods than at 50 periods. J. F. S.

The Gold Numbers of Protalbic and Lysalbic Acids. ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1920, **42**, 595—597). —The gold numbers of protalbic and lysalbic acids, determined by Zsigmondy's process (A., 1903, i, 135), are 0·15—0·20 and 0·10—0·125 respectively. Comparison of these with those for dextrin (125—150), soluble starch (10—15), sodium oleate (2—4), egg-albumin (0·08—0·10), and gum arabic (0·10—0·125) suggests that the protective action of the acids in question has been much overrated. J. K.

The Coagulation of Clay Suspensions and Silicic Acid. OTTO M. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 460—472).—The experiments recorded were made with the object of determining the action of electrolytes commonly occurring in natural waters on the stability of colloidal clay suspensions and silicic acid held in solution, and their effect when aluminium sulphate is used as a coagulant. Experiments on the precipitation of silicic acid by alkalis in the presence of aluminium salts showed that the optimum hydrogen-ion concentration for the precipitation of the aluminium hydroxide and the removal of the silicic acid is 1×10^{-8}. The limiting values of the hydrogen-ion concentration between which the solid aluminium hydroxide phase is present are 1×10^{-4} and 1×10^{-11}. If the alkali (sodium hydroxide) is added all at once, the presence of silicic acid prevents the precipitation of aluminium hydroxide, apparently by acting as a protective colloid. The presence of bivalent cations, however, destroys this protective power. The effect of a number of electrolytes on the coagulation of clay suspensions by aluminium sulphate was studied. The electrolytes examined, arranged in their order of efficiency as coagulants, were: aluminium sulphate, calcium and barium hydr-

oxides, calcium chloride, magnesium sulphate, magnesium and calcium hydrogen carbonates. The ratio of efficiency of aluminium to calcium and barium ions is about 5 to 1. Sodium hydroxide, hydrogen carbonate, carbonate, and sulphate have a singular influence on the coagulating effect of aluminium sulphate. With a given amount of sodium hydroxide, for example, and gradual addition of aluminium sulphate to the clay suspension, there is first increased dispersion, then coagulation, followed by renewed dispersion and a second coagulation. The second disperse phase is not as stable as the first. The presence of silicic acid has in all cases a retarding effect on the coagulation by aluminium sulphate, whatever salts may be present. E. H. R.

Emulsions. III. T. R. Briggs [with J. C. Ashmead, C. F. Tears, and L. H. Clark] (*J. Physical Chem.*, 1920, **24**, 120—126. Compare A., 1915, ii, 531).—The time required to emulsify a series of mixtures of benzene and 1% solutions of sodium oleate has been determined for various methods of mixing. Mechanical shaking, intermittent hand shaking, with measured interval between the shakes, continuous hand shaking, and rolling the bottles containing the mixtures were compared. It is shown that intermittent shaking is far more efficient than uninterrupted shaking, even in a shaking machine. The time and number of shakes required to complete an emulsification both vary with the rest interval between the shakes. Emulsions are easily made by rolling or rotating cylindrical bottles containing oil and soap solution. This method of procedure is similar to the "Continental" method (see following abstract). The ideal emulsifying process is one causing the benzene to break up into drops with the least disintegration of the aqueous soap solution. J. F. S.

Emulsions. IV. T. R. Briggs, F. R. Du Cassé and L. R. Clark (*J. Physical Chem.*, 1920, **24**, 147—160).—The preparation of emulsions by the continental method is investigated in the case of olive oil. The method consists in preparing an emulsion nucleus by grinding together in a mortar definite quantities of oil, water, and gum, and then diluting with the requisite quantity of water. It is shown that the hypothesis of Roon and Oesper (A., 1917, ii, 299) that hydration of an emulsifying colloid must take place at the moment of disintegrating the oil is not in accordance with experiment. Even in a mortar, emulsions may be made with previously hydrated colloids. Emulsions are easily produced by the method of trituration in a mortar if the area of the interface between oil and water is made sufficiently large. One method by which this may be achieved is to suspend finely divided solids, which are easily wetted, in the oil. The effectiveness of the solid is increased by decreasing the average size of the particles. Up to a certain limit, the readiness with which an emulsion forms increases as the quantity of solid added. It is preferable to suspend the solid in the liquid before adding the

dispersing solution. The most effective solids are those readily wetted by the dispersion medium. In the continental method, gum arabic (acacia) plays the part of finely divided solid and emulsifying colloid. The finely divided solid serves to increase the interface between oil and water. Wetting phenomena may also cause the displacement of one liquid by the other, and consequently give rise to disintegration of the displaced liquid. Emulsions of water in oil may be made in a mortar in the presence of finely divided solids easily wetted by oil. J. F. S.

Physical Chemistry of Rusting. II. Equilibria in the System Lead–Sulphur–Oxygen. W. Reinders (*Zeitsch. anorg. Chem.*, 1919, **109**, 52—62. Compare A., 1915, ii, 47, 773).—A criticism of a paper by Schenck and Albers (A., 1919, ii, 222) on the equilibria in the system lead–sulphur–oxygen, in which it is shown that the experimental results are not trustworthy and will not bear the interpretation put on them. Of the five quintuple points characterised, two are shown to be impossible, and five other equilibrium curves are also not in keeping with known facts.

J. F. S.

Chemical Affinity. XI. The Transformation of Reciprocal Pairs of Salts and the Equilibrium of Benzidine and Benzidine Sulphate. J. N. Brönsted and Agnes Petersen (*K. Danske. Vidensk. Medd. Math. Phys.*, 1917, **1**, No. 3, 1—21; from *Chem. Zentr.*, 1920, i, 425—426. Compare A., 1915, ii, 221).—The affinity of the reaction $KCl + NaBr \longrightarrow KBr + NaCl$ has been estimated to be 1620 cal. by an electrochemical method, using hydrogen, tartaric acid, and alkali tartrates; the following elements were measured: (1) $H_2 | H_2C_4H_4O_6, KHC_4H_4O_6, KCl | HgCl, Hg$; (2) $H | H_2C_2H_4O_6, NaHC_4H_4O_6, H_2O, NaCl | HgCl, Hg$; (3) $H | H_2C_4H_4O_6, KHC_4H_4O_6, KBr | HgBr, Hg$;

(4) $H | H_2C_4H_4O_6, NaHC_4H_4O_6, H_2O, NaBr, 2H_2O | HgBr, Hg$.

The affinity of the transformation $KCl + \frac{1}{2}Na_2SO_4 \longrightarrow \frac{1}{2}K_2SO_4 + NaCl$ was measured in the following manner. As a consequence of the formation of glaserite, the system of the three salts is unstable, but the two systems $KCl + K_2SO_4$ and $NaCl + Na_2SO_4$ are separately completely stable. If sulphuric acid of the same potential is added to each system, the following actions occur: $\frac{1}{2}H_2SO_4 + KCl = \frac{1}{2}K_2SO_4 + HCl$ and $\frac{1}{2}H_2SO_4 + NaCl = \frac{1}{2}Na_2SO_4 + HCl$; hydrochloric acid is thus liberated at two potentials, the difference of which is a measure of the affinity of the change. The two potentials were measured by hydrogen and calomel electrodes. The authors endeavoured to secure equality in the sulphuric acid potential in the two systems by the addition of a mixture of benzidine and benzidine sulphate, or of the latter alone; it was expected that elimination of sulphuric acid would occur in accordance with the scheme $C_{12}H_8(NH_2)_2, H_2SO_4 \longrightarrow C_{12}H_8(NH_2)_2 + H_2SO_4$ until the solution had attained a sulphuric acid potential independent of the other components. It was, however, found

that the decomposition of benzidine sulphate by water or aqueous solutions does not take place in such a simple manner, since the addition of benzidine to a solution which was in equilibrium with benzidine sulphate caused a marked decrease of the sulphuric acid potential. Further investigation disclosed the existence of the *compounds* $[C_{12}H_8(NH_2)_2]_3,2H_2SO_4$ and $[C_{12}H_8(NH_2)_2]_2,H_2SO_4$ in addition to the well-known sulphate. By the aid of elements, in which the sulphuric acid potential was maintained constant in the manner indicated, the affinity of the reaction $KCl + \frac{1}{2}Na_2SO_4$ was estimated to be 210 cal. H. W.

The Term "Inversion." J. B. FERGUSON (*Science*, 1919, [N.S.], **50**, 544—546).—The following terminology in inorganic chemistry is suggested. Changes such as the passage of rhombic to monoclinic sulphur, the equilibrium temperatures of which are fixed at fixed pressures, regardless of the complexity of the system, provided no solid solutions are formed, are examples of "inversion." Such reactions as the melting of sodium sulphate decahydrate, which occur, under a definite pressure, within a range of temperatures in presence of a third component, are cases of "transition." "Dissociation" is the name given to univariant changes when the compositions of all the phases can be represented by chemical formulæ. J. R. P.

Proportions of Chlorine and of Hydrogen which Limit the Explosion of Mixtures of these Gases. PAUL MATHIEU (*J. Physique*, 1917, **7**, 166—172).—If a mixture of hydrogen and chlorine is exposed to the radiation from the spark of an induction coil, explosion occurs only when the composition of the mixture is between the limits 91·9% of chlorine and 8·1% of hydrogen and 14·3% of chlorine and 85·7% of hydrogen. When exposed to the radiation of a magnesium flame, the explosive mixtures lie between the limits 90·2% of chlorine and 9·8% of hydrogen and 47·5% of chlorine and 52·5% of hydrogen. The different explosion limits are possibly due to the good conductivity of hydrogen for heat. CHEMICAL ABSTRACTS.

Hydrolysis of Esters of Polyhydric Alcohols. II. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, **40**, 667—680).—In this paper are given the experimental data obtained in connexion with the equation previously deduced for the hydrolysis of triacetin to glycerol (this vol., ii, 170). CHEMICAL ABSTRACTS.

Catalysis. VII. Catalysis in Heterogeneous Systems. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 570—575).—The velocity of solution of anhydrous ferric sulphate in water can be increased by the presence of reducing agents, such as stannous chloride or ferrous sulphate, but no satisfactory explanation of this phenomenon is forthcoming.

When 20% nitric acid in excess acts on copper at 18°, so that

the whole of the copper is dissolved, the action is accelerated by both ferrous and ferric salts, as well as by a number of other salts and compounds. The view hitherto held regarding the part played by ferrous salts in destroying nitrous acid needs to be modified, since it has been shown that nitrous acid is formed by the action of nitric acid on ferrous salts. Oxidising agents like hydrogen peroxide, potassium permanganate, chromic acid, etc., which destroy nitrous acid, retard the action of nitric acid on copper. Finally, there is a small group of substances which in very small concentrations exert a slight accelerating effect, whilst in large concentrations they have a retarding effect (compare T., 1917, **111**, 707). W. G.

The Effect of Surface Oxidation on some Metallic Catalysts. FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1920, 42, 402—411).—The observation reported by Wigand (*Sitzungsber. Ges. Naturwiss. Marburg*, 1907, p. 33) that platinum foil which has been used as an electrode acquires an increased catalytic activity towards detonating gas (electrolytic hydrogen–oxygen mixture) has been confirmed by the author. The increased activity, however, is confined to the anode; it is due to surface oxidation, and can be induced by chemical means as well as by anodic polarisation. The surface oxidation probably consists in the formation of a film of surface-combined oxygen of atomic dimensions. Increase of catalytic activity by anodic polarisation was also found in the case of palladium and of gold; in the case of cobalt, a slight increase detected was probably due to increase of the active surface by etching. An estimation of the comparative order of magnitudes of the activities of the metals examined gives 50:1 for the ratio of palladium to platinum, 2000:1 for platinum to gold, and 200:1 for platinum to cobalt. The results obtained contradict Sackur's conclusions with regard to the effect of polarisation on the catalytic activity of metals (A., 1906, ii, 261). E. H. R.

Do Simple Numerical Relationships Exist between the Linear Dimensions of the Atoms? MARIANO PIERUCCI (*Nuovo Cim.*, 1920, [vi], **19**, i, 109—115).—The author assumes that only at the absolute zero of temperature is it possible for the atomic volume to represent the true volume of the atoms. On this assumption, he calculates the cube root of the atomic volume at absolute zero for those elements which (1) have a known density in the solid state, and (2) have a coefficient of thermal expansion which either is known at low temperatures or is known and very small at ordinary temperatures. To this cube root he gives the name *atomic radius*. The necessary data are taken from Landolt's tables, and are known, in some instances only approximately, for twenty-nine elements. The results obtained appear to suggest that the atomic radii of all elements are integral multiples of one and the same length. T. H. P.

Electron Ring Model and the Electrical Moment of some Dipolar Molecules. LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 156—158. Compare this vol., ii, 172).—The electrical moment (M) of diatomic molecules is considered theoretically, and equations are developed by which this factor, and other factors connected with the structure of molecules, may be calculated. Calculations are carried out for the molecules of carbon monoxide, hydrogen chloride, water, and carbon dioxide, and the following values obtained; h is the distance between the two nucleii of effective charge number n_1 and n_2, respectively, and mass m_1 and m_2; r_1 and r_2 are the distances of the nuclei from the mechanical centre of gravity, and d_1 and d_2 their distances from the electron ring; a is the radius of the ring of n electrons, ω is the angular velocity of the electrons in the ring, which is calculated from the quanten equation $na^2\omega = kh/2\pi$, where the quanten number k for the second and third ring is equal to 2; x is the fraction of h where the electrical centre of gravity of the ring lies, and yh is the distance the electrical centre of gravity of the nucleus lies from the nucleus n, that is, $y = n_2/n$; l is the length of the dipole, and the other symbols have their usual meaning. Carbon monoxide, $P = 10{\cdot}07 \times 10^{-40}$, $Q = 10{\cdot}07 \times 10^{-40}$, $n_1 = 6$, $n_2 = 4$, $h = 0{\cdot}951 \times 10^{-8}$, $r_1 = 0{\cdot}4075 \times 10^{-8}$, $r_2 = 0{\cdot}5435 \times 10^{-8}$, $x = 0{\cdot}184$, $y = 0{\cdot}400$, $d_1 = 0{\cdot}175 \times 10^{-8}$, $d_2 = 0{\cdot}776 \times 10^{-8}$, $a = 0{\cdot}713 \times 10^{-8}$, $\omega = 4{\cdot}60 \times 10^{16}$, $l = 0{\cdot}205 \times 10^{-8}$, and $M = 9{\cdot}70 \times 10^{-18}$. Hydrogen chloride, $P - Q = 2{\cdot}7 \times 10^{-40}$, $n_1 = 7$, $n_2 = 1$, $h = 1{\cdot}31 \times 10^{-8}$, $r_1 = 0{\cdot}036 \times 10^{-8}$, $r_2 = 1{\cdot}274 \times 10^{-8}$, $x = 0{\cdot}0034$, $y = 0{\cdot}125$, $d_1 = 0{\cdot}0045 \times 10^{-8}$, $d_2 = 1{\cdot}3055 \times 10^{-8}$, $a = 0{\cdot}786 \times 10^{-8}$,

$$\omega = 3{\cdot}78 \times 10^{16},$$

$l = 0{\cdot}159 \times 10^{-8}$, $M = 6{\cdot}02 \times 10^{-18}$. Water, $P = 2{\cdot}21 \times 10^{-40}$, $Q = 1{\cdot}25 \times 10^{-40}$, $R = 0{\cdot}96 \times 10^{-40}$, $n_1 = 6$, $n_2 = 1$, $h = 0{\cdot}657 \times 10^{-8}$, $b = 0{\cdot}542 \times 10^{-8}$, $r_1 = 0{\cdot}0734 \times 10^{-8}$, $r_2 = 0{\cdot}796 \times 10^{-8}$, $x = 0{\cdot}027$, $y = 0{\cdot}250$, $d_1 = 0{\cdot}0177 \times 10^{-8}$, $d_2 = 0{\cdot}639 \times 10^{-8}$, $a = 0{\cdot}402 \times 10^{-8}$, $\omega = 14{\cdot}4 \times 10^{16}$, $l = 0{\cdot}146 \times 10^{-8}$, $M = 1{\cdot}87 \times 10^{-18}$. Carbon dioxide, $P = 9{\cdot}40 \times 10^{-40}$, $Q = 5{\cdot}83 \times 10^{-40}$, $R = 3{\cdot}57 \times 10^{-40}$, $n_1 = 4$, $n_2 = 6$, $h = 0{\cdot}708 \times 10^{-8}$, $b = 0{\cdot}262 \times 10^{-8}$, $r_1 = 0{\cdot}515 \times 10^{-8}$, $r_2 = 0{\cdot}325 \times 10^{-8}$, $x = 0{\cdot}90$, $y = 0{\cdot}75$, $d_1 = 0{\cdot}637 \times 10^{-8}$, $d_2 = 0{\cdot}071 \times 10^{-8}$,

$$a = 0{\cdot}485 \times 10^{-8},$$

$\omega = 9{\cdot}92 \times 10^{-16}$, $l = 0{\cdot}106 \times 10^{-8}$, $M = 8{\cdot}01 \times 10^{-18}$. J. F. S.

Twenty-sixth Annual Report of Committee on Atomic Weights. Determinations Published during 1918 and 1919. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1920, **42**, 327—333).—Papers published during 1918 and 1919 dealing with atomic weight determinations are summarised. E. H. R.

Arrangement of Electrons in the Elements of the Long Periods. RUDOLF LADENBURG (*Naturwiss.*, 1920, **8**, 5—11; from *Chem. Zentr.*, 1920, i, 315—316).—The arrangement of electrons postulated by Kossel (A., 1919, ii, 408) gives satisfactory results as far as scandium. For elements of higher atomic weight, how-

ever, it must be replaced by another conception, since it demands a definite prevalent valency, whilst the elements from titanium to zinc and from zirconium to cadmium exhibit a series of mobile valency stages, and, also, the maximal valency, so far as such can be spoken of, does not increase from member to member, but remains constant. Peculiar physical properties, such as magnetism of the elements and colour of the elementary ions, are associated with the change in chemical behaviour. Both properties are dependent on conditions under which the readily separable outermost valency electrons are already detached. Those elements which are paramagnetic and have small atomic volumes yield coloured, positively charged ions in the dissolved state and in glasses and precious stones. To account for the peculiar position of the elements of the series mentioned above, the author considers that the outermost zone of all the elements from titanium to zinc and from yttrium to cadmium (except copper and silver), contains two electrons. The common metallic character of the majority of these elements, and the fact that they are at least positively bivalent in their heteropolar compounds, thereby find their expression. The sharp maxima of the atomic volumes of the alkali metals indicate that with them a new electron zone commences; this is certainly not the case with copper, silver, and gold, the atomic volumes of which lie near the minima, and are scarcely to be distinguished from the neighbouring elements. The new electrons of the elements titanium, vanadium, chromium, etc., must migrate into the interior of the outermost zone, but are supposed to form an intermediate zone between the two outer ones previously described, since they can participate in chemical reactions in the same manner as the electrons of the outermost zone, but have greater freedom of motion than these, and can also be separated singly; an explanation of the varying valency of these elements is thus given. In the cases of zinc and cadmium, in which the number of electrons in the intermediate zone is already increased to ten, a stable arrangement similar to that of the noble gases is postulated, so that an electron of this zone cannot be detached in exchange with other atoms. In the cases of gallium and indium, the new electrons take their place in the outer zones (as in the short periods), which in the corresponding rare gases (krypton and xenon) contain eight electrons. The assumption of the intermediate zones facilitates the understanding of the relationship between the colour of the ions and the periodic system. It is thereby assumed that the electrons of the intermediate zone, when the latter is incomplete and contains less than ten electrons, are more readily displaced by the energy of visible light, and, in accordance with Bohr's conception of emission and absorption, absorb the corresponding energy and pass to a path of greater energy. Absorption in the ultra-violet must be accomplished by electrons of other, more complete zones. Although an analogy must exist between the colour of the ions and the variable valency, since each property is ascribed to the looseness of the attachment

of the electrons in the incomplete intermediate zone, a complete agreement between these properties is not to be expected. The connexion between colour and ability to form compounds depends on the amounts of energy which are required for the absorption of light on the one hand, and for the production of another degree of combination on the other. The quantities of energy are related in the same manner as the resonance potential and ionisation tension in the line spectra of metals. Doubtless, coloured compounds can exist in which the intermediate zone is absent, but mobility of the electrons is due to other influences. The simultaneous appearance of colour in the ions and of paramagnetism in the periodic scheme indicates that the latter is also caused by the electrons of the intermediate zone, although it is acknowledged that the latter phenomenon is but little understood. The distinctive characteristics of the electrons of the magnetic elements are still less obvious, and are not expressed in the author's scheme. The latter is, however, only to be regarded as a preliminary conception. H. W.

New Periodic Relationship between the Atomic Weights of the Chemical Elements. KARL FEHRLE (*Physikal. Zeitsch.*, 1920, **21**, 162—166. Compare A., 1918, ii, 296).—A theoretical paper in which, on the basis of the quantum theory, an expression is evolved whereby the atomic weight of the elements may be calculated. The calculation is based on the atomic model previously described by the author (*loc. cit.*). The atomic weight is calculated by means of the formula $A=\Sigma_1^n \sqrt[7]{67{\cdot}7+(n-1)16{\cdot}59}$, where n is the number of sheaths in the atom. The calculated atomic weights run parallel with the experimental values, and the difference between the two is a periodic function of the atomic weight. The cause of this periodic function is to be found in the characteristic vibrations of the molecule in relationship to those of its atoms. J. F. S.

Inter-relationship of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1920, **120**, 169—170).—The author has picked out nine pairs of elements, the sum of the atomic weights of each pair of which approximate to that of vanadium; six pairs, the sum of the atomic weights of which approximate to that of chromium; and eight pairs, the sum of the atomic weights of which approximate to that of manganese. In these tables, three sets of coincidences are apparent: (i) The sum of the valencies of each pair is equal to the valency of the element under consideration in seventeen cases out of twenty-three. (ii) The sum of the valencies of each pair is odd or even according as the valency of the element under consideration is odd or even. (iii) The sum of each pair of atomic weights is greater than the integer which is nearest to the atomic weight of the element under consideration in twenty cases out of twenty-three, when the atomic weight of oxygen is taken as sixteen, and is less than the same in nineteen cases out

of twenty-three when hydrogen is taken as the unit. It is shown that the probability that the first coincidence is due to chance is one to several billions, that the second is a chance or accident is one to eight millions, and that the third is a chance or accident is one to four thousand millions. The author concludes, therefore, that these relationships are due to some general similarity in the formation of the elements. [See also A., 1919, ii, 106.]

J. F. S.

Dependence of the Valency Number on Temperature. III. The Systematic Doctrine of Affinity. X. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1919, **109**, 132—144. Compare A., 1915, ii, 440, 465, 466).—A theoretical paper in which the dependence of the valency exercised by various elements at different temperatures is considered. The dissociation of the higher chlorides of gold, platinum, iridium, and vanadium, the oxides of iron, uranium, and lead, the crystalline hydrates of uranyl nitrate and certain sulphides is discussed, and the dissociation represented as valency isobars. From this consideration it is shown that the valency isobars are steeper the lower the temperature of the starting point. This rule, however, is not absolute, for when substances which have dissimilar constitution are considered, it fails entirely. The constitutive influences are considered in connexion with the metal ammines. The temperature range over which the ammines of the chlorides of the metals manganese, iron, cobalt, and nickel are stable is tabulated. In the case of the hexammines, that of nickel iodide has the greatest temperature range of existence (177·5°), and that of manganese chloride the least. The order of existence increases from manganese to iron, cobalt, and nickel, and from chloride to bromide and iodide. In the case of the diammines, the range of existence increases from chloride to bromide, and falls again to the iodide to a value lower than that for the chloride; it also increases from manganese to iron, and then falls to cobalt and nickel. It is found in the monammines that the existence range falls from chloride to iodide and from manganese to nickel. J. F. S.

Calculation of the Chemical Constants of Polyatomic Gases from the Planck Theory of Probabilities. LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 156—159. Compare this vol., ii, 172).—It is shown that the strict calculation from the Planck probability theory leads to the same result as the Sackur-Tetrode calculation (*loc. cit.*). It is shown that $\sqrt[3]{PQR}=0\cdot94\times10^{-40}$ for water according to the Sackur-Tetrode calculation, but from the rotation spectrum, according to Planck's first theory, the value is $1\cdot38\times10^{-40}$, and from the Planck second theory $2\cdot48\times10^{-40}$. No reason can, as yet, be given for the discrepancy.

J. F. S.

Graphic Mixture Calculations. WA. OSTWALD (*Chem. Zeit.*, 1920, **44**, 241—242).—When it is required, from two or more

materials containing two or more constituents in known proportions, to produce another mixture containing the same constituents in other proportions, the calculation can be greatly simplified by the use of the graphic method. In more complicated cases, an exact solution of the problem may be impossible, and the graphic method then affords a ready means of obtaining an approximate solution. E. H. R.

Measurements of the Volume of the Mercury Meniscus. J. Palacios (*Anal. Fis. Quim.*, 1919, **7**, 275—295).—Exact determinations have been made of the volume occupied by the meniscus of mercury in glass tubes 5, 6, 7, 8, 9, 10, and 11 mm. in diameter, and with heights of meniscus varying by 0·1 mm. from 0·1 mm. to 2·1 mm. The author draws attention to a constant appreciable difference between his results and those of Scheel and Heuse (*Ann. Physique*, 1910, **33**, 291), and suggests that an error of 0·04 mm. for the radius of the tube used by Scheel and Heuse would account for the discrepancies. W. R. S.

Apparatus for the Extraction of Liquids. Kurt Brauer and Erwin W. Ebert (*Chem. Zeit.*, 1920, **44**, 214).—An apparatus of the Soxhlet type is described for the extraction of a liquid with a solvent of greater density. In place of the usual siphon of the apparatus, a tube is provided extending upwards from the bottom of the main cylinder and entering the side (vapour) tube at about two-thirds the height of the latter. As the heavy solvent collects below the liquid undergoing extraction, it flows gradually back through the side-tube into the extraction flask. A tap is provided between the cylinder and stem of the apparatus. W. P. S.

Lecture Experiment on Combustion. A. Price (*Chem. News*, 1920, **120**, 149—150).—A Bunsen burner is made with a long, wide glass tube in place of the usual metal tube, and a little above the top of the tube a wire is clamped at right angles to it. The gas is turned on so that a mixture of coal-gas and air ascends the tube, as in the ordinary Bunsen burner. By carefully lowering a small flame on to the wire, with possibly a little adjustment of the gas supply, the gas can be made to burn indefinitely from the top of the wire with a very pale blue, luminous flame. The flame can similarly be made to burn from a small, rounded object, such as a bullet, suspended above the tube by a fine wire. The continuance of the phenomenon depends on the mixed gases coming up the tube at a certain velocity, too great for combustion to take place at the end of the tube. The presence of the wire or small object lowers the velocity sufficiently to permit the gases to burn. When the velocity is lowered sufficiently by cutting off the gas supply, the flame strikes back to the jet at the bottom of the tube. E. H. R.

Inorganic Chemistry.

The Purification of Liquefied and Compressed Gases for Laboratory Purposes. L. MOSER [and, in part, W. FOLTZ] (*Zeitsch. anorg. Chem.*, 1920, **110**, 125—142).—An account is given of the impurities likely to be present in those gases which are supplied commercially in cylinders, and of the best means for purifying the gases. Carbon dioxide, which is obtained commercially by heating a metal hydrogen carbonate solution, contains 1—2% of impurity. It can be completely freed from oxygen by passing it at a rate of 4 to 6 litres per hour through a paste of chromium acetate, and then through a 15% solution of titanous chloride acidified with hydrochloric acid, or by passing over red-hot copper at 4 to 10 litres per hour. Carbon monoxide can be removed by passing the gas over asbestos carrying finely divided cuprous oxide at 700—800°, hydrogen sulphide by copper sulphate on pumice stone, and sulphur dioxide by a solution of potassium permanganate. Commercial nitrogen, prepared by the Linde process, has only to be freed from traces of oxygen. The best wet absorbent is copper gauze in ammonium carbonate solution, the gas being subsequently passed through concentrated sulphuric acid to absorb ammonia. It can finally be passed over copper asbestos at 700—800° to remove the last trace of oxygen. Electrolytic hydrogen is practically pure, but that prepared from water gas by the Linde process may contain air, oxides of carbon, and sometimes arsine. Further, through the action of the carbon monoxide on the steel cylinder under pressure, iron pentacarbonyl is formed, and the hydrogen may contain more than 3% of it. Owing to the difficulty of removing this impurity or the carbon monoxide formed by its decomposition, such hydrogen is unsuitable for laboratory use. Commercial oxygen, prepared by the Linde process, contains only traces of nitrogen, which cannot be removed by chemical means, and a trace of carbon dioxide, which can be removed by soda-lime. Electrolytic oxygen may contain as much as 4% of hydrogen, which can be burnt to water by passing the gas over heated platinised asbestos. Commercial chlorine, generally of electrolytic origin, can be freed from air and oxides of carbon by liquefying in a tube immersed in a mixture of ether and carbon dioxide and redistilling, and commercial sulphur dioxide can be purified in the same way, although it is pure enough for most purposes. Commercial ammonia contains about 2% of impurity, consisting of water and organic substances, such as pyridine, methylamine, and pyrrole. The gas can be dried by means of lime or soda-lime, but the organic impurities are difficult to remove. E. H. R.

Determination of the Boiling Point of Sulphur by means of the Nitrogen Thermometer. P. CHAPPUIS (*Bur. Int. Poids. Mes.*, 1917, *Mem.* **16**, 44 pp.).—The b. p. of sulphur at normal

pressure, determined by measuring the increase of pressure at constant volume of nitrogen (prepared from a solution of sodium nitrite, ammonium sulphate, and potassium chromate, and washed with a mixture of potassium dichromate and sulphuric acid and then with potassium hydroxide) in a silica bulb of capacity approximately 247 c.c., was found to be 444·60° on the thermodynamic scale.

The original paper should be consulted for details of the apparatus employed and the corrections made.

CHEMICAL ABSTRACTS.

Action of Hydroxylamine on Sodium Tetrathionate. A. GUTMANN (*Ber.*, 1920, **53**, [*B*], 444—446).—In acid solution, hydroxylamine oxidises the sulphite residue in tetrathionic acid to sulphuric acid, and is itself reduced to ammonia, $H_2S_4O_6 + NH_2{\cdot}OH + H_2O = 2H_2SO_4 + 2S + NH_3$. In alkaline solution, on the other hand, the loosely combined oxygen atom of the tetrathionate oxidises hydroxylamine to nitrous or nitric acid, $Na_2S_4O_6 + 2NH_2{\cdot}OH + 3NaOH = 2Na_2S_2O_3 + NaNO_2 + 3H_2O + NH_3$.

H. W.

The Decomposition Equilibrium of Nitrosyl Bromide and the Proof of (the Formation of) the Tribromide, $NOBr_3$. MAX TRAUTZ and VASANJI P. DALAL (*Zeitsch. anorg. Chem.*, 1920, **110**, 1—47).—A continuation of previous work (A., 1918, ii, 162). The equilibrium between nitric oxide, bromine, and their reaction products was studied between $-15°$ and $330°$ by the method previously described (compare Trautz and Wachenheim, A., 1917, ii, 74), with bromine pressures between 13 and 500 mm., and nitric oxide pressures between 28 and 900 mm. Equilibrium is attained very rapidly, and the reaction is the most rapid which has yet been studied. For low bromine pressures, below 50 mm., and at temperatures above 140°, the amount of the tribromide formed appears to be negligible, and the reaction $2NO + Br_2 \rightleftharpoons 2NOBr$ can be regarded as of the third order. As is to be expected from the small heat of reaction, the reaction is more rapid than the formation of nitrosyl chloride. The velocity constant is, at $-15°$, $k = 1{\cdot}1 \times 10^{-10}$.

An independent proof of the existence of nitrosyl bromide and nitrosyl tribromide was obtained from an investigation of the fusion-point diagram of the reaction products of bromine and nitric oxide. The fusion curve shows a eutectic of bromine and nitrosyl tribromide, a maximum at $-40°$ corresponding with $NOBr_3$, a second eutectic of $NOBr_3$ and NOBr in the neighbourhood of $-60°$, and a second maximum corresponding with NOBr at about $-55°$. Nitrosyl tribromide was found to be a brownish-black, almost opaque liquid which begins to boil, with partial decomposition, at about 32°. It has $D_4^{20} = 2{\cdot}637$, which agrees closely with Landolt's value, 2·628 at 22·6°. The fusion diagram does not confirm or exclude the existence of nitrosyl dibromide

among the products. The heats of formation of the mono- and tri-bromide were calculated from measurements made of their heats of reaction in aqueous solution with potassium hydroxide. The significance of the results obtained cannot be exactly estimated, because the extent of decomposition of liquid NOBr and $NOBr_3$ is unknown, but probably the heat of formation of NOBr is between 9000 and 10,500 cal., and of $NOBr_3$ between 22,000 and 27,000 cal., at 22°. The results obtained for the equilibrium constants and for the heats of formation agree, in general, with theory. It is concluded that, in liquid mixtures of the components at low temperatures, the principal product is nitrosyl tribromide, in gaseous mixtures rich in bromine at moderate temperatures, nitrosyl dibromide, and under other conditions, nitrosyl bromide or its decomposition products.

E. H. R.

War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes. JAMES WALKER (T., 1920, **117**, 382—389).—A lecture delivered before the Chemical Society on December 18th, 1919.

Interaction of Phosphorus Haloids and Arsenious and Arsenic Compounds. NAGENDRA NATH SEN (*J. Proc. Asiatic Soc. Bengal*, 1919, **15**, 263—265).—When a few drops of phosphorus trichloride are added to an aqueous solution of arsenious oxide, the solution turns yellow, then opaque-brown, and finally a copious precipitate of arsenic is thrown down. The arsenic is amorphous, apparently a new allotropic form, insoluble in carbon disulphide. The reaction does not take place when phosphorous acid is used or when the phosphorus trichloride is first dissolved in water. With phosphorus tribromide and tri-iodide, the same reaction takes place, but more slowly, and in the latter case the precipitate is contaminated with red phosphorus. Unlike the trichloride, the tribromide and tri-iodide still bring about the reaction if they are first dissolved in water. It appears, therefore, that an intermediate compound is first formed when the phosphorus haloid dissolves in water, but that, in the case of the trichloride, this intermediate compound is more rapidly decomposed than in the cases of the other haloids. The reduction, which takes place with both arsenites and arsenates, is brought about by the intermediate compound. The reaction is very delicate, and with phosphorus trichloride the presence of 0·000075 gram of arsenic per c.c. can be detected. Antimonious and antimonic compounds do not give the reaction. The course of the reduction is probably given by the equation $As_2O_3 + 3PCl_3 + 9H_2O = 2As + 3H_3PO_4 + 9HCl$. E. H. R.

Coagulation of Metal Sulphide Hydrosols. II. Influence of Temperature on the Rate of Coagulation of Arsenious Sulphide Hydrosols. JÑANENDRA NATH MUKHERJEE (T., 1920, **117**, 350—358).

Charcoal before the War. I. WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 127—146).—A theoretical paper in which the composition and structure of various forms of charcoal are discussed. J. F. S.

Some Properties of Charcoals. H. E. CUDE and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 391—401).—When the density of charcoal is determined by the water immersion method, a gradual increase in weight of the immersed charcoal is observed, the maximum weight only being reached after many days. The same occurs when other liquids, such as carbon disulphide, benzene, or carbon tetrachloride, are used instead of water, and in each case the final density found for the charcoal is different. Quantitative experiments were made with a sample of cocoanut charcoal, 18—20 mesh, and the maximum densities found were: with water, 1·854; with carbon disulphide, 1·984; with benzene, 1·797; and with carbon tetrachloride, 1·647. The change in weight of the immersed charcoal with time is due to the progressive penetration of the liquid into the charcoal, rapidly at first, then more slowly. The rate of penetration and the final density found appear to vary in proportion to the surface tension and inversely with the viscosity of the liquid. The smaller the size of grain of the charcoal, the greater is the density found, and with the smallest grains obtainable, 0·001 mm. in diameter, using water as the liquid, the final density 1·900 was obtained. High pressure causes rapid penetration, and the 18—20-mesh charcoal in water under 8600 atm. gave a density of 1·902 in the course of a comparatively short time. E. H. R.

Activation of Wood-charcoal by Heat Treatment. JAMES C. PHILIP, SYDNEY DUNNILL, and OLIVE WORKMAN (T., 1920, **117**, 362—369).

Oxidation of Carbon Monoxide. KARL HOFMANN (D.R.-P 307614; from *Chem. Zentr.*, 1920, ii, 446).—The process is effected by chromic acid solution to which mercuric oxide has been added. The presence of the latter substance so accelerates the oxidation of carbon monoxide that this gas can be removed from its mixtures with air and other gases with sufficient rapidity for analytical and hygienic purposes. H. W.

Carbonyl Chloride. E. PATERNÒ and A. MAZZUCCHELLI (*Gazzetta*, 1920, **50**, i, 30—53).—The carbonyl chloride was prepared by the action of fuming sulphuric acid on carbon tetrachloride, and was purified by distillation with the help of a dephlegmator maintained at constant temperature. A special apparatus was designed for storing the chloride obtained and for delivering small amounts of it as required.

The density of liquid carbonyl chloride, measured by means of a dilatometer with a graduated capillary tube at temperatures

between $-15{\cdot}4^\circ$ and $+59{\cdot}9^\circ$, is expressed well by the formula $D=1{\cdot}4264-0{\cdot}002326t$, t being in degrees Centigrade.

Determinations have been made of the orthobaric density of liquid carbonyl chloride and its vapour by means of Ter-Gazarian's modification (A., 1906, ii, 423) of Young's process, the temperatures employed lying between $60{\cdot}3^\circ$ and $181{\cdot}6^\circ$. In accordance with the rectilinear diameter law of Cailletet and Mathias, the sum of the densities of the liquid and vapour varies very nearly linearly with the temperature, the maximum divergences being less than 0·3%. The whole of the results agree well with the expression $1{\cdot}4277-0{\cdot}00214t$, whilst for temperatures above 111°, for which the diameter is more certainly rectilinear, the formula $1{\cdot}4380-0{\cdot}0022t$ holds.

Comparison of the orthobars of carbonyl chloride and *n*-pentane (see Young, T., 1897, **71**, 455) gives for the critical temperature of carbonyl chloride the value 187°, which should be accurate to within 1—2°. The two expressions given above then lead to the respective values 0·5137 and 0·5133 for the critical density. The conclusions arrived at by Young from considerations based on the law of the rectilinear diameter show that for carbonyl chloride this diameter is convex towards the axis of temperature, and also lead to the provisional value 51·5 atmos. for the critical pressure. According to Mathias, the extrapolated density at absolute zero is three times the critical density, but for carbonyl chloride, such extrapolated density, calculated in accordance with Mendeléev's formula, is almost exactly four times the critical density.

Measurements of the surface tension of carbonyl chloride have been made by means of Ramsay and Shields' method (T., 1893, **63**, 1094), the values obtained for $\gamma=ga^2(d-\sigma)/2$ being 19·51 at 16·7°, 17·10 at 34·5°, and 15·42 at 46·1°. The so-called molecular tension, $G=\gamma(M/S)^{\frac{2}{3}}$, has the mean value 2·05, which agrees well with the value 2·12 given by Ramsay for non-polymerised compounds.

Various series of measurements of the vapour pressure at temperatures ranging from about -23° to $+25^\circ$ have been made, the results being in satisfactory agreement with the formula $\log p=7{\cdot}5995-1326/T$, p being the absolute pressure in mm. of mercury at the latitude of Rome and T the absolute temperature. This formula indicates the boiling point of carbonyl chloride to be 8·02°/760 mm., whereas Beckmann (*Zeitsch. anorg. Chem.*, 1907, **55**, 371) found 8·2°/756 mm.

Berthelot's statement that carbonyl chloride dissolves unaltered to the extent of 2—3 vols. in water, and that it reacts with the latter only slowly, has been contested by recent authors (compare Grignard and Urbain, A., 1919, ii, 340). The authors find that the chloride cannot exist for an appreciable time in contact with pure water, but that the products, carbon dioxide and hydrochloric acid, which it forms with the water hinder further action: in the case of gaseous carbonyl chloride, the carbon dioxide forms an inert separating layer at the surface of the liquid, whilst with

liquid carbonyl chloride it is saturation with hydrogen chloride of the water in immediate contact with the liquid to which retardation of the reaction is due. The action is therefore dependent essentially on diffusion.

Retardation of the reaction between carbonyl chloride and water is caused by acids in general. Attempts made to measure the velocity of the reaction in presence of sulphuric acid by measuring the volumes of carbon dioxide evolved in different periods of time led to irregular results, but showed that the reactivity of sulphuric acid solutions with carbonyl chloride diminishes continuously with increase in the concentration of the sulphuric acid and with fall in the temperature. No hypothesis is advanced to explain this effect of acids, which is due, undoubtedly, to a true retardation of the reaction, and not to a displacement of the equilibrium.

The reaction between carbon tetrachloride and fuming sulphuric acid is not limited to that expressed by the equation $CCl_4 + 2SO_3 = S_2O_5Cl_2 + COCl_2$, since in presence of excess of the hot fuming acid, the reaction $CCl_4 + 4SO_3 = 2S_2O_5Cl_2 + CO_2$ takes place.

If kept at a temperature below 0°, liquid carbonyl chloride absorbs gaseous chlorine in large proportions. At $-15°$ and under the ordinary pressure, a golden-yellow liquid containing 28·3% of free chlorine is formed; the vapour pressures of this liquid at different temperatures exhibit satisfactory agreement with the law stating that, in mixtures of similar and non-polymerised liquids, the partial pressure of any component is equal to the pressure of the pure component multiplied by its molecular percentage in the mixture.

Carbonyl chloride is absorbed in considerable proportions by heavy lubricating oils, from which it is expelled rapidly and almost completely by a current of air. T. H. P.

The Production of Helium and Neon in Discharge Tubes containing Hydrogen. Arnaldo Piutti and Ettore Cardoso (*Gazzetta*, 1920, **50**, i, 5—23).—The authors have carried out a number of experiments on the action of the discharge between aluminium electrodes on hydrogen prepared by the electrolysis of dilute sulphuric acid and carefully purified. By means of the spectroscope employed, the neon contained in 0·05 c.c. of air could be detected with ease. After the subjection of the hydrogen to the action of the discharge, the gas was burnt in oxygen prepared by heating potassium permanganate and carefully purified before use; the burnt gases were extracted and purified, and the residue examined spectroscopically. The apparatus used is briefly described. The pressure maintained during the discharge, which occupied from one to twelve hours, varied in different experiments between 0·1 mm. and 3 mm., the temperature prevailing being also varied in different cases.

In no single case was the formation of helium or neon in the tubes detectable, this result being in agreement with that of Strutt

(A., 1914, ii, 201) and in contradiction to that of Collie, Patterson, and Masson (A., 1914, ii, 847; compare Baly, Annual Report, 1914, 45). T. H. P.

The Solubility of Potassium Bromide in Bromine Water. ALFRED FRANCIS JOSEPH (T., 1920, **117**, 377—381).

Formation of Mixed Crystals of Potassium and Ammonium Nitrates at the Ordinary Temperature. CAILLART (*Bull. Soc. franç. Min.*, 1918, **41**, 21—30; from *Chem. Zentr.*, 1920, i, 358).—The work is an extension of that of Wallerant (A., 1906, ii, 151), who has investigated the formation of the mixed crystals from the molten salts. The method suffers particularly from the drawback that the crystals remain in a metastable condition outside the limits of their stability. The author has therefore investigated the crystals deposited from aqueous solutions at a constant temperature, 17°. Difficulties are encountered owing to the great disparity in the solubilities of the salts and to the poor development of the mixed crystals rich in ammonium nitrate, which almost prevents measurement. Crystallographic methods are therefore supplemented by optical ones. The solubility curves of mixtures of the two salts, and the graphs showing the relationship between the composition of the mixed crystals and that of the mother liquors, have been studied in particular, and are found to be composed of three segments corresponding with three types of mixed crystals: (1) rhombic crystals of the potassium nitrate type containing 0—17·2 molecules of ammonium nitrate per 100 molecules of mixture, (2) monoclinic crystals with 55—94·5 molecules of ammonium nitrate per 100 molecules of mixture, and (3) rhombic crystals of the ammonium nitrate type with 98—100 molecules of ammonium nitrate per 100 molecules of mixture. Two types of mixed crystals separate at each concentration, corresponding with the two points of intersection of the curves. H. W.

Influence of Various Metals on the Decomposition of Sodium Amalgam by Water. ERICH MÜLLER and ALFRED RIEDEL (*Zeitsch. Elektrochem.*, 1920, **26**, 104—109).—The rate of decomposition of water by 0·2% sodium amalgam in the presence of metallic and other substances has been determined. The amalgam (80 grams) was rapidly stirred with 50 c.c. of water and a piece of the metal in question, and the hydrogen collected and measured. The experiments were carried out with ferro-molybdenum, cast iron, wrought iron, iron carbide, silicon, ferro-silicon, ferro-vanadium, ferro-tungsten, chromium, platinum, palladium, iridium, nickel, cobalt, manganese, tantalum, graphite, and ferric oxide. It is shown that the iron alloys of molybdenum, vanadium, tungsten, and chromium have a very strong catalytic action on the process. This action depends on the increase in the surface of the amalgam due to the solution, and subsequent separation of the metals. The possibility of applying this action to

the manufacture of sodium hydroxide by the mercury electrode process is considered, and it is shown that if the finely divided catalyst can be entirely removed from the mercury at the end of the process, then it will be advantageous to add the catalyst to the electrolyte in the mercury cells, but if it is not possible to entirely remove the catalyst, then the total current will not be used in the formation of amalgam, but a portion will be used in the liberation of hydrogen. J. F. S.

Behaviour of Magnesium Nitride towards Carbon Monoxide and Carbon Dioxide. FR. FICHTER and CHRISTOPH SCHÖLLY (*Helv. Chim. Acta*, 1920, **3**, 298—304).—The statement of Briegleb and Geuther (1862) that magnesium nitride reacts with carbon monoxide and carbon dioxide to give magnesium oxide, cyanogen, and carbon, and, in the latter case, nitrogen also, is erroneous. Quantitative experiments show that the decomposition of the freshly prepared nitride at 1250° in a stream of the respective gases is expressed by the following equations: $Mg_3N_2 + 3CO_2 = 3MgO + 3CO + N_2$ and $Mg_3N_2 + 3CO = 3MgO + N_2 + 3C$. Carbon monoxide causes no change at 750°, and reacts less readily than carbon dioxide. The reactions are considered to follow on the dissociation of the nitride, which was shown to be almost complete at 1500°. Aluminium nitride, which dissociates much less readily (Fichter and Oesterheld, A., 1915, ii. 168), is oxidised by carbon dioxide at 1300° only to the extent of 89%. Briegleb and Geuther's statement may have been due to confusion of hydrocyanic acid with cyanogen, since the authors observed a transient odour of the former from the product of the action of carbon monoxide on magnesium nitride. It is suggested in explanation of this that magnesium cyanide may have been produced to a slight extent by a reaction analogous to that by which calcium nitride is converted into the cyanide by the action of carbon and nitrogen. J. K.

The Reactions of the Metallurgy of Zinc. M. LEMARCHANDS (*Compt. rend.*, 1920, **170**, 805—807).—From a study of the interaction of zinc oxide and carbon in an atmosphere of nitrogen, it is shown that zinc oxide is readily reduced directly by carbon without the necessary intermediate formation of carbon monoxide. The amount of carbon entering into the reaction is intermediate between the amounts necessary for the two possible actions $ZnO + C = Zn + CO$, $2ZnO + C = 2Zn + CO_2$. This is explained on the grounds that the reduction of zinc oxide by carbon monoxide, $ZnO + CO = Zn + CO_2$, takes place with a velocity superior to that of the reduction of carbon dioxide by carbon. This is possible, since the first action commences at 350°, and the second only at 400°. Further, for any given temperature, the vapour pressure of zinc oxide is much greater than that of carbon. W. G.

Lead Chromate. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1919, **109**, 226—234).—When lead acetate is treated with an equi-

valent quantity of potassium chromate, a slightly basic lea chromate is precipitated, the relationship between lead oxide an chromic acid being represented by $PbO:CrO_3::1\cdot104:1$; if, how ever, 20 c.c. of N-potassium chromate are added to 19 c.c. of N-lea acetate, a light yellow precipitate is produced which, on stirring changes to an orange-yellow, crystalline precipitate of normal lea chromate. When 40 c.c. of N-lead acetate are mixed with 10 c.c of N-potassium chromate, and the mixture evaporated to dryne on the water-bath and then washed with hot water, a basic lead chromate of the composition $PbO,PbCrO_4$ is obtained. Rubbing 2 grams of normal lead chromate with 30 c.c. of N-potassium acetate solution, evaporating to dryness on a water-bath, and then washing with water, yields a double lead potassium chromate, $2PbCrO_4,K_2CrO_4,H_2O$. J. F. S.

Copper Silicon Alloys. A. SANFOURCHE (*Rev. Met.*, 1919, 16, 246—256; from *Chem. Zentr.*, 1920, i. 409).—The alloys were prepared from electrolytic copper containing only 0·00007% of iron, and crystalline silicon, which after treatment with nitric and hydrofluoric acids left only 0·52% of residue and was free from iron; in spite of this, however, the alloys contained iron derived from the tubes, which seldom exceeded 0·25% in amount. The preparation of the alloys, the analytical methods, and the apparatus are shortly described, whilst the phase diagram and the results of microscopical and chemical investigation of the alloys are fully discussed. Rudolfi (A., 1907, ii, 352) has attributed the observed maximum (12·10% Si) to the formation of a compound, Cu_9Si (Cu = 87·04%, Si = 12·96%), but the difference in the silicon content exceeds the experimental error, whilst, also, the accuracy of his curve is greatly affected by the small number of alloys investigated. The formula $Cu_{18}Si_4$ (Cu = 87·91%, Si = 12·09%), on the other hand, is in good agreement with the results obtained. The effect of this compound and of Rudolfi's substance, $Cu_{19}Si_4$, on the formation of β- and γ-crystals is considered in the light of the phase diagram, and the possibility of the assumption of solid solutions instead of definite compounds is discussed. Since it is impossible to alloy more than 12·10% of silicon with copper, all the formulæ of copper–silicon alloys requiring a higher silicon content are to be deleted from the literature. H. W.

Amalgams. GIOVANNA MAYR (*Nuovo Cim.*, 1920, [vi], 19, i, 116—128).—The authoress gives a brief summary of previous work on the constitution of amalgams, and from the results of her own experiments, not described in detail, the following conclusions are drawn. When the chemical constitution of an amalgam is known, determination of the *E.M.F.* of a concentration cell furnishes a means of deducing the ratio between the concentrations of the two amalgams forming the cell. During the passage of a current through an amalgam, the metal dissolved in the mercury is transported towards the anode, that is, in the direction of the negative current. As regards such transport, no appreciable distinction is

evident (1) between metals, such as thallium, which give rise to compounds with the mercury, and those, such as zinc, which dissolve as such in mercury, or (2) between metals, such as sodium and potassium, which increase the resistance of the mercury, and those, such as zinc, which diminish the resistance. Thus, in contradiction to Lewis's view (compare Lewis, Adams, and Lanman, A., 1916, ii, 76), such transport of the metal does not appear to be related to the increase or decrease of the resistance of the mercury produced by dissolution of the metal. Increase in the resistance of mercury may depend on the specific resistance of mercurides formed by the dissolved metal. T. H. P.

Colourless Variety of Mercuric Iodide. G. Tammann (*Zeitsch. anorg. Chem.*, 1920, **109**, 213—214).—A colourless variety of mercuric iodide may be obtained as follows: a quantity (10—15 grams) of mercuric iodide is placed in a long tube, sealed at one end and connected with a large vessel at the other, and heated at 300—350°. The pressure is suddenly reduced to 0·1 atm., when mercuric iodide condenses in the large vessel as a white snow, which in a few seconds becomes rose-coloured, and in a few minutes has changed to the stable vermilion form of mercuric iodide. If the large vessel is previously cooled, the white form may be preserved for longer periods. The yellow variety of mercuric iodide becomes colourless at the temperature of liquid air. J. F. S.

The Solubility of Mercuric Oxide in Sodium Hydroxide Solutions. G. Fuseya (*J. Amer. Chem. Soc.*, 1920, **42**, 368—371).—To determine whether a compound can possibly be formed through the interaction of mercuric oxide and sodium hydroxide, solubility determinations of the former were made in sodium hydroxide solutions of different concentrations at 25°. The solubility curves, in which concentration of mercuric oxide is plotted against sodium hydroxide and hydroxyl-ion concentrations, respectively, when extrapolated to zero concentration of hydroxide or hydroxyl ion, give a value for the solubility of mercuric oxide considerably above the normal solubility in pure water. It is considered probable that the normal solubility is that of the red form of the oxide, whilst the extrapolated value represents that of the more finely divided yellow form. The steady increase of the solubility of mercuric oxide as the concentration of sodium hydroxide increases indicates that the hydrated oxide functions as a very weak acid. The ionisation constant of the first hydrogen of mercuric acid, H_2HgO_2, is calculated to be $1{\cdot}7\times10^{-15}$. E. H. R.

Scandium. II. Jan Štěrba-Böhm (*Bull. Soc. chim.*, 1920, [iv], **27**, 185—195. Compare A., 1914, ii, 565).—A study of scandium fluoride and certain of its double salts. Scandium fluoride, as prepared by Crookes's method (compare A., 1908, ii, 695), is not pure, because of the absorption of impurities during the precipitation. The fluoride may be obtained in a pure state

by the action of hydrofluoric acid on scandium oxide, the product being finally heated at 150—180° to remove any free hydrogen fluoride. Fluoroscandic acids do not exist in the free state, but three ammonium scandifluorides were prepared. The ammonium scandifluoride, $(NH_4)_3ScF_6$ (compare Meyer, A., 1914, ii, 369), undergoes hydrolysis in water, giving first the *compound*, $(NH_4)_2ScF_6$, quadratic crystals, and then the *compound*, $(NH_4)ScF_4$, as a microcrystalline powder. The first compound is only obtained by hydrolysis in the presence of ammonium fluoride; in warm or cold water alone the second compound is always obtained.

A small quantity of a crystalline *silver scandifluoride* was obtained by dissolving scandium fluoride in a concentrated solution of silver fluoride. W. G.

Light Reactions of Cerium Dioxide. CARL RENZ (*Zeitsch. anorg. Chem.*, 1920, **110**, 104—106).—Pure cerium dioxide, which has a pale yellow colour, is unaffected by light, but if mixed with a small quantity of praseodymia or terbia it becomes light-sensitive. Such a mixture, which has a slightly reddish-yellow colour, when exposed to sunlight becomes bluish-grey, but in the dark its original colour is restored. In the cerite earths, cerium is known to have an oxidising influence on praseodymia, and apparently in sunlight this influence becomes emphasised. Discussing the position of the rare earth metals in the periodic system of the elements, the author expresses the view that, in the building up of the system, these elements are the counterpart of the transition members of the radioactive series in the degradation of the system. E. H. R.

The Rare Earths. X. The Purification and Atomic Weight of Samarium. A. W. OWENS, C. W. BALKE, and H. C. KREMERS (*J. Amer. Chem. Soc.*, 1920, **42**, 515—522).—The samarium material used for these experiments was obtained from the Welsbach Mantle Co., and consisted of rare earth residues from monazite sand after extraction of most of the cerium. The cerium remaining was first removed by treatment of the nitrates with bromine. Lanthanum, praseodymium, and neodymium were removed by fractionation of the rare earth magnesium double nitrates, first from aqueous solution and then from nitric acid. Europium and gadolinium were removed by fractionation of the rare earth magnesium nitrates with bismuth magnesium nitrate, the samarium material used for the atomic weight determinations being taken from the middle series of the last fractionations. The final purification consisted in the alternate precipitation of the samarium material as hydroxide and oxalate, and five recrystallisations as hydrated chloride. Attempts to determine the atomic weight from the oxide–chloride ratio were abandoned, owing to the impossibility of obtaining pure oxide. The ratio hydrated chloride–anhydrous chloride was also found unsatisfactory, because of the difficulty of obtaining pure samarium chloride hexahydrate.

Finally, the anhydrous chloride–silver ratio was used, by determining the weight of silver, as nitrate, needed to precipitate the whole of the chlorine from a known weight of anhydrous samarium chloride, the end-point being determined by means of the nephelometer. A mean of eighteen determinations gave 150·43 as the atomic weight of samarium (Ag, 107·88), the extremes being 150·40 and 150·49. E. H. R.

Gadolinium. Methods of Separation of the Terbium and Ytterbium Earths. R. J. Meyer and Ulrich Müller (*Zeitsch. anorg. Chem.*, 1919, **109**, 1—30).—A number of methods of separating gadolinium from the rare earths occurring in euxenite have been examined and the efficiency of the separations compared. The alkali double sulphate method is only of use for separating a mixture which contains gadolinium into two parts, one of which contains the whole of the gadolinium. The hydrazine double sulphate method effects separation in the same way as the alkali double sulphate method, but it has the advantage of being more easily controlled. Fractional crystallisation of the bromates effects an extremely good separation of the terbium earths from the ytterbium earths, but the cerium earths cannot be separated from the terbium earths because the solubility of gadolinium bromate lies between that of samarium and neodymium bromate. Consequently, this method must be used along with another to bring about the required separation. The fractional crystallisation of the acetates effects a rapid separation of gadolinium from samarium and didymium. The great value of this method lies in the fact that it is the complement of the bromate method, and an alternation of these with the double nitrate method, which fractionates in the opposite direction, brings about a good separation. Crystallisation of the formates fractionates in the same sense as the bromates, so that a combination of the formate and acetate methods is capable of yielding pure terbium earths. Crystallisation of the double manganese nitrates, whilst very good for the separation of the cerium and yttrium earths, is found to be of very little use in separating a small amount of cerium earths from a large amount of gadolinium. Bismuth double nitrates, however, will effect this separation, and by this means a specimen of very pure gadolinium oxide was prepared. Crystallisation of the nitrates effects a fairly rapid separation of the cerium earths from gadolinium, but towards the end of the fractionation the separation becomes incomplete The method is far inferior both in ease of manipulation and in efficiency to the acetate method. Gadolinium and terbium are easily separated by the fractional precipitation with ammonia.

The following hydrazine rare earth double sulphates have been prepared and are described: *Lanthanum hydrazine sulphate*, $La_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O$, separates in sparingly soluble, colourless crystals on warming a solution of the mixed sulphates to 75°. *Neodymium hydrazine sulphate*, $Nd_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O$, is formed in reddish-violet crystals, which separate on warming a

solution of the mixed sulphates. *Gadolinium hydrazine sulphate*, $Gd_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O$, separates in colourless, sparingly soluble crystals when a solution of the mixed sulphate is boiled for a considerable time. *Yttrium hydrazine sulphate*,

$$Y_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O,$$

is prepared by concentrating a solution of the mixed sulphates until crystallisation takes place. It is very soluble in water. *Scandium hydrazine sulphate*, $Sc_2(SO_4)_3,3(N_2H_5)_2SO_4$, is a very soluble compound which forms good crystals.

The solubility of several acetates of the rare earths has been determined in water; the following values, in grams per 100 grams of saturated solution at 25°, are given: lanthanum, 14·47; praseodymium, 21·48; neodymium, 20·76; samarium, 13·05; gadolinium, 10·37; and yttrium, 8·28. The best starting materials for the preparation of gadolinium compounds are: euxenite, samarskite, or the monazite residues, but in any case the preparation should be commenced with several kilos of material.

The following method of procedure is recommended for the purification of gadolinium compounds: (1) If the rare earth mixture contains little cerium earths and much yttrium earths the gadolinium is separated with the cerium earths in one operation by the potassium double sulphate method. (2) If the mixture contains much cerium earths the major portion of these is separated by the double nitrate method. In either case a fraction very much richer in gadolinium is obtained. This is converted into the bromates and the yttrium earths removed by fractionation. Hereby the ytterbium earths first pass into the mother liquors, then follow the erbium earths, and last of all yttrium. It is essential that the yttrium should be removed at this point, for it is scarcely possible to separate it at any of the succeeding stages. The main fraction contains samarium, gadolinium, neodymium, terbium, and europium; it is converted into acetate and fractionated, the fractionation being combined with the fractionation of the double bismuth nitrates. The cerium earths are rapidly separated, and a brown mixture of oxides, containing gadolinium and terbium, is obtained. These two elements are rapidly separated by fractional precipitation with ammonia. It is possible, by the above method, to obtain pure gadolinium oxide in a few months. J. F. S.

Ammonia Derivatives of the Haloids of Bivalent Manganese and Iron. WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1919, **109**, 89—110).—The ammonia derivatives of ferrous and manganous chloride, bromide, and iodide have been investigated, some new derivatives have been prepared, and the dissociation pressure and curves of the various products have been determined for a number of temperatures. Anhydrous manganous chloride rapidly absorbs ammonia at the temperature of solid carbon dioxide and alcohol to form the hexa-ammine, $MnCl_2,6NH_3$, which is a pure white compound. At 76·5° the isothermal falls a little and then remains horizontal until the com-

position falls to that of the diamine, where the pressure falls suddenly to the value for this compound. The isothermal for the equilibrium $MnCl_2,2NH_3 \rightleftarrows MnCl_2,NH_3 + NH_3 \rightleftarrows MnCl_2 + 2NH_3$ has been determined at 229°, and indicates the existence of the monammine. No other ammines of manganous chloride exist in equilibrium with ammonia in the temperature and pressure range examined. The following dissociation pressures (p) and heat of dissociation (Q) have been calculated from the experimental results: hexammine, 59°, p=218 mm.; 63°, p=258 mm.; 76·5°, p=495 mm.; Q=12·6K (mean); diammine, 181°, p=65 mm., Q=18·7K; 206°, p=196 mm., Q=18·8K; 230°, p=407 mm., Q=19·1K; monammine, 215°, p=9·4 mm., Q=22·1K; 230°, p=28 mm., Q=21·75K; 278°, p=95 mm., Q=22·7K. Manganous bromide forms similar ammines to the chloride; the following values have been calculated from the isothermals: hexammine, 107°, p=305 mm., Q=14·26K; diammine, 182°, p=13·7 mm., Q=20·2K; 215°, p=56·4 mm., Q=20·4K; 230°, p=98·0 mm., Q=20·5K. In the case of manganous iodide, the hexammine and diammine alone exist; the isothermals indicate the non-existence of a monammine; the following values are calculated: hexammine, 154°, p=316 mm., Q=16·2K; diammine, 208°, p=11·1 mm., Q=21·6K; 215°, p=14·6 mm., Q=21·7K. By similar dissociation experiments ferrous chloride is shown to form a monammine in addition to the hexammine and diammine already known. The following values for the ferrous chloride ammines are obtained: hexammine, 90°, p=270 mm., Q=13·65K; diammine, 230°, p=121 mm., Q=20·3K; 277°, p=555 mm., Q=20·7K; monammine, 214·5°, p=5·8 mm., Q=22·5K; 277°, p=54·4 mm., Q=23·1K. Ferrous chloride also forms a pure white, voluminous compound with six molecules of methylamine and a grey compound with two molecules of methylamine. Ferrous bromide absorbs ammonia rapidly at ordinary temperatures to form a white hexammine, which dissociates at elevated temperatures into a dirty white diammine, and this into a dark grey monammine. The following data are calculated from the isotherms: hexammine, 107°, p=126 mm., Q=14·9K; diammine, 215°, p=11·5 mm., Q=21·9K; 230°, p=23·5 mm., Q=21·9K; 277°, p=126 mm., Q=22·3K; monammine, 215°, p=5·7 mm., Q=22·6K; 230°, p=9·7 mm., Q=22·8K; 277°, p=61·5 mm., Q=23·1K. In the case of ferrous iodide a monammine does not exist; the following values are obtained for the other two ammines: hexammine, 153°, p=206 mm., Q=16·5K; diammine, 215°, p=6·1 mm., Q=22·5K; 231°, p=12·1 mm., Q=22·6K; and 278°, p=85·4 mm., Q=22·8K. All the measurements and calculated values are compared with those of Ephraim (A., 1912, ii, 546; 1914, i, 17; 1913, ii, 129) and Girardet (A., 1911, ii, 43). J. F. S.

Non-rusting Iron. Hanns Fischer (*Chem. Zeit.*, 1920, **44**, 242).—A discussion on the ancient pillar of Northern India which, after 3000 years, is quite free from rust. A satisfactory explanation of the phenomenon is not yet forthcoming. E. H. R.

Cobaltammines. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 576—579. Compare A., 1913, ii, 319; 1914, ii, 57).—The preparation of cobaltammines is guided by the law of mass action, and thus depends on the concentration of the reacting substances. A nitro-group in a compound may be replaced by an amino-group by warming the compound with a mixture of ammonium hydroxide and an ammonium salt, whilst the reverse change is brought about when the salt is warmed with a nitrite solution.

The hydrolysis of purpureo-cobalt chloride to give aquopentamminecobalt chloride,

$$\left[Co\begin{matrix}(NH_3)_5\\Cl\end{matrix}\right]Cl_2 + H_2O \rightleftharpoons \left[Co\begin{matrix}(NH_3)_5\\H_2O\end{matrix}\right]Cl,$$

is catalytically accelerated by the presence of hydroxyl ions.

The hydroxides of the cobaltammines may be prepared in solution by treating the corresponding haloid with moist silver oxide, but purpureo-cobalt chloride under these conditions gives aquepentamminecobalt hydroxide. W. G.

The Constitution of Two Cobaltammines. PAUL JOB (*Compt. rend.*, 1920, **170**, 731—734).—Titration of roseo-cobaltic sulphate by barium hydroxide, the action being followed by electrical conductivity measurements, shows that the action takes place in two stages. The curve has two singular points, the first corresponding with the precipitation of one-third of the sulphuric acid and the second with its complete precipitation. These results support Werner's view as to the constitution of the roseo-cobalt salts, the changes being given by

$$\left[Co\begin{matrix}(NH_3)_5\\H_2O\end{matrix}\right]_2(SO_4)_3 + Ba(OH)_2 = \left[Co\begin{matrix}(NH_3)_5\\(OH)\end{matrix}\right]_2(SO_4)_2 + BaSO_4 + 2H_2O$$

$$\left[Co\begin{matrix}(NH_3)_5\\(OH)\end{matrix}\right]_2(SO_4)_2 + 2Ba(OH)_2 = \left[Co\begin{matrix}(NH_3)_5\\(OH)\end{matrix}\right]_2(OH)_4 + 2BaSO_4.$$

The author has isolated the intermediate *compound*,

$$Co(NH_3)_5(OH)SO_4,2H_2O,$$

in a crystalline form.

In the same way diroseo-cobalt sulphate when titrated with barium hydroxide gives a singular point when two-thirds of the sulphuric acid is precipitated, and another when the whole of it is precipitated. W. G.

Green Double Salts of Chromium Chlorides. NILS LARSSON (*Zeitsch. anorg. Chem.*, 1920, **110**, 153—165).—A number of new double salts formed by monochloroaquochromium chloride,

$$[CrCl(H_2O)_5]Cl_2,$$

and dichloroaquochromium chloride, $[CrCl_2(H_2O)_4]Cl$, with chlorides and sulphates of different bases have been prepared. The double salts correspond in colour with the simple chromium compounds, the dichloro-compounds being light green and the monochloro-compounds light bluish-green. The compounds of the former class

are more hygroscopic, and, in general, less readily soluble than those of the latter. In all the compounds described containing the sulphate radicle, the whole of this radicle is precipitated by barium nitrate, and is therefore outside the complex chromium radicle. The following compounds were prepared.

Double Salts with Sulphates.– (1) Dichlorochromi-compounds: $[CrCl_2(H_2O)_4]Cl,2(NH_4)_2SO_4,2H_2O$; $[CrCl_2(H_2O)_4]_2SO_4,3(NH_4)_2SO_4$; $[CrCl_2(H_2O)_4]_2SO_4,(NH_4)_6H_2(SO_4)_4$; tetramethylammonium compound, $[CrCl_2(H_2O)_4]SO_4,(NMe_4)_2SO_4,3H_2O$; methylammonium compounds, $[CrCl_2(H_2O)_4]_2SO_4,3(NH_3Me)_2SO_4$;

$$[CrCl_2(H_2O)_4]_2SO_4,(NH_3Me)_6H_2(SO_4)_4;$$

tetraethylammonium compound,

$$[CrCl_2(H_2O)_4]_2SO_4,(NEt_4)_2SO_4,10H_2O;$$

ethylammonium compound, $[CrCl_2(H_2O)_4]_2SO_4,(NH_3Et)_2SO_4,6H_2O$; guanidine compounds, $[CrCl_2(H_2O)_4]_2SO_4,3(CN_3H_6)_2SO_4$;

$$[CrCl_2(H_2O)_4]_2SO_4,(CN_3H_6)_6H_2(SO_4)_4;$$

pyridine compound, $[CrCl_2(H_2O)_4]_2SO_4,(C_5NH_6)_2SO_4,4H_2O$.

(2) Monochlorochromium compounds: ammonium compounds, $[CrCl(H_2O)_5]Cl_2,(NH_4)_2SO_4,H_2O$, $[CrCl(H_2O)_5]SO_4,(NH_4)_2SO_4$; $[CrCl(H_2O)_5]SO_4,(NH_4)HSO_4$; methylammonium compound, $[CrCl(H_2O)_5]SO_4,(NH_3Me)_2SO_4$; dimethylammonium compound, $[CrCl(H_2O)_5]SO_4,(NH_2Me_2)_2SO_4$; tetramethylammonium compound, $2[CrCl(H_2O)_5]SO_4,(NMe_4)_2SO_4$; ethylammonium compound, $2[CrCl(H_2O)_5]SO_4,(NH_3Et)_2SO_4,4H_2O$; hydroxylamine compounds, $2[CrCl(H_2O)_5]Cl(SO_4)_{\frac{1}{2}},(NH_4O)_2SO_4,2H_2O$, and

$$[CrCl(H_2O)_5]SO_4,NH_2\cdot OH,H_2SO_4;$$

pyridine compound, $2[CrCl(H_2O)_5]SO_4,(C_5H_6N)_2SO_4$; strychnine compound, $2[CrCl(H_2O)_5]SO_4,(C_{21}H_{23}N_2O_2)_2SO_4$.

Double Salts with Chlorides.—Rubidium compound,

$$[CrCl_2(H_2O)_4]Cl,2RbCl,$$

stable in air, heated at 85°, loses three molecular proportions of water and changes into Neuman's salt, $[CrCl_5(H_2O)]Rb_2$; ammonium compound, $[CrCl(H_2O)_5]Cl_2,NH_4Cl,H_2O$; rubidium compound, $[CrCl(H_2O)_5]Cl_2,RbCl$; cæsium compound, $[CrCl(H_2O)_5]Cl_2,CsCl$. No potassium salt could be prepared, but a very hygroscopic lithium salt was obtained. E. H. R.

Chromi-aquo-triammines. Fr. Frowein (*Zeitsch. anorg. Chem.*, 1920, **110**, 107—124).—Conductivity measurements have been made on the three compounds, dichloromonaquotriammin-chromichloride, $[Cr(NH_3)_3Cl_2H_2O]Cl$; monochlorodiaquotriammin-chromichloride, $[Cr(NH_3)_3Cl(H_2O)_2]Cl_2$; and triaquotriammin-chromichloride, $[Cr(NH_3)_3(H_2O)_3]Cl_3$. Three isomerides of the monoaquo-compound have been described by Seemann (*Inaug. Diss.*, 1910, p. 27), but, of these, only the chloride I was examined. The compounds were prepared by Seemann's methods with slight modifications. The monaquo-compound gradually passes over in solution into the diaquo-, and this, in turn, into the triaquo-compound, and on this account it was necessary to make the conductivity measurements on the freshly prepared solutions. The

changes can be followed by the change of colour of the solution, that of the monoaquo-compound being blue, that of the diaquo reddish-violet, and that of the triaquo red. These changes are more rapid the more dilute the solutions. The conductivity of the monoaquo-compound is lowest, that of the triaquo-compound highest, so that the change is accompanied by a gradual increase in conductivity of the solution. No direct transformation of the mono- into the tri-aquo-compound occurs, but the diaquo-compound is always the first hydration product of the monoaquo. It is concluded from the measurements that the compounds contain no water outside the inner sphere, that is, they are purely co-ordinated compounds. The solution of the triaquo-compound undergoes slow decomposition, the conductivity curve first showing a maximum, followed by a minimum. Deposition of chromium hydroxide eventually takes place, but intermediate complex compounds are probably first formed. E. H. R.

Recovery of Ammonium Molybdate from Residues, etc., obtained in Estimating Phosphoric Acid by Lorenz's Method. H. NEUBAUER and E. WOLFERTS (*Zeitsch. anal. Chem.*, 1919, **58**, 445—448).—The filtrates, precipitates, etc., obtained in Lorenz's method (A., 1901, ii, 278) are partially neutralised with ammonia, and the molybdic acid is precipitated at 80° by the addition of an excess of sodium phosphate; the yellow precipitate is collected, dissolved in ammonia, the phosphoric acid precipitated by the addition of magnesium nitrate, the precipitate removed, and the filtrate concentrated. Ammonium molybdate crystallises out, and is purified by recrystallisation, first from very dilute ammonia solution, and then from water. W. P. S.

The Uranyl Radicle as a Chromophore. ARNO MÜLLER (*Zeitsch. anorg. Chem.*, 1919, **109**, 235—274).—The colour of a large number of uranyl salts is considered; the colour is, in general, yellow, but the presence of hydroxyl or keto-groups, particularly in the *a*- or ortho-positions, displaces the colour strongly towards the red. The benzene nucleus also acts strongly in displacing the colour towards the red end of the spectrum, particularly when the uranyl group is directly connected with phenolic oxygen. The author has tabulated the formulæ, crystal system, melting point, solubility in water, alcohol, and ether, and colour of fifty-five monocarboxylic, dicarboxylic, hydroxy-carboxylic, phenolcarboxylic, and polycarboxylic acid salts of the uranyl group. The method of preparation and the properties of fifty-two uranyl salts of aromatic and aliphatic acids of various types are described. J. F. S.

Some Compounds of Zirconium and the Hydrolysis of its Salts. ED. CHAUVENET (*Ann. Chim.*, 1920, [ix], **13**, 59—86).—A résumé of work already published (compare A., 1914, i, 321; 1917, ii, 264, 321, 322, 374, 416; 1918, ii, 234, 269, 321). W. G.

Alloys of Gold and Silicon. CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 111—114).—Warren (A., 1893, ii, 474) and Vigouroux (A., 1896, ii, 600) have shown that gold forms an alloy with silicon. The author has studied the diagram of state of the system gold, of 0·999 purity and silicon containing 4—5% of impurity, mostly iron, being used. Fusion and cooling of the mixtures were carried out in a rapid current of hydrogen. Owing to the low thermal conductivity of silicon, the duration of the arrests of the cooling was very irregular, and yielded no information. The cooling results show that gold and silicon are miscible in all proportions in the liquid condition, that they form no compounds, and that they are non-miscible in the solid state, at any rate within the limits of the experimental accuracy attained. The eutectic alloy melts at 370°. With the alloy containing 85% of silicon, no retardation corresponding with the solidification of the eutectic is observable, but microscopic examination reveals crystals of gold scattered throughout the mass; the formation of mixed crystals at this concentration is therefore excluded. Almost all the alloys rich in silicon exhibit at the surface a golden-yellow globule, which is sharply detached from the greyish-blue, metallic block, and contains a greater proportion of gold than the mixture from which it is formed. A similar globule has been observed with silicon–silver alloys (compare Arrivaut, A., 1908, ii, 1035) and with silicon–aluminium alloys (compare Fraenkel, A., 1908, ii, 592), and its formation is certainly due to the fact that silicon solidifies with increase of volume. Hence, during the solidification, the part which solidifies last, namely, the eutectic, is forced upwards and forms the globule.

The melting point of gold is lowered by about 800° by 6—7% of silicon.

Microscopic examination of the alloys fully confirms the results of the thermal analysis. T. H. P.

Ammonium Pentahalogenoruthenates. A. GUTBIER (*Zeitsch. anorg. Chem.*, 1919, **109**, 187—212).—Polemical. A criticism of statements as to ruthenium and its double chlorides in a paper by Mylius and Mazzucchelli (A., 1915, ii, 491), in which it is shown that the method of preparation of ammonium pentachlororuthenate suggested by these authors is not capable of giving this compound. [See also Gutbier and Trenkner, A., 1905, ii, 463.]

J. F. S.

Mineralogical Chemistry.

Bismutoplagionite, a New Mineral. EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **49**, 166—168).—A lead-grey, indistinctly fibrous mineral associated with pyrites, quartz, etc., was sent from Wickes, Montana. The streak is dark brownish-grey; D 5·35, H 2·8. The mineral is completely soluble in hot concentrated hydrochloric acid, whilst the pyrites is only slightly attacked. In the analysis (I), the sulphur was estimated by difference, the iron being assumed to represent pyrites; the insoluble portion also consisted mainly of pyrites. Deducting these impurities, the recalculated composition II agrees with the formula $5PbS,4Bi_2S_3$, in which a small amount of the bismuth is replaced by antimony.

	PbS.	FeS_2.	Sb_2S_3.	Bi_2S_3.	Insoluble.	As_2S_3,CuS,Ag_2S.	Total.
I.	30·21	1·25	3·37	45·62	18·88	traces	99·33
II.	38·13	—	4·26	57·61	—	—	100·00

The ratio $PbS:R_2S_3$ being the same as in plagionite,
$(5PbS,4Sb_2S_3)$,
the mineral is placed in the plagionite group, together with liveingite $(5PbS,4As_2S_3)$, rather than with galenobismutite (PbS,Bi_2S_3). L. J. S.

Hæmatite and Rutile formed by the Action of Chlorine at High Temperatures. H. E. MERWIN and J. C. HOSTETTER (*Amer. Min.*, 1919, **4**, 126—127).—In the course of experiments on the removal of iron from clay pots by leading chlorine into the covered pots, heated in a gas-fired furnace at 1000—1100°, when they were removed from the furnace directly after the chlorine treatment, a deposit of hæmatite crystals was found on the outer, upper portion of the pot where chlorine and vaporised ferric chloride had come into contact with the products of combustion of the furnace. The crystals were in the form of rhombohedra with perfect faces. On the inside of one of the pots were found crystals of rutile in the form of very thin, twinned plates. The formation of crystals of hæmatite and rutile from vapours containing ferric chloride or titanium chloride has been previously recorded.

E. H. R.

Calcite from New York State. H. F. GARDNER (*Amer. Min.*, 1920, **5**, 3—5).—Enormous crystals (180 kilos.) of calcite of a dull lavender or violet colour were obtained from a cave in a limestone quarry at Sterlingbush, Lewis Co., N.Y. These have been grouped as a cave in the New York State Museum at Albany, and by transmitted lamp light show a deep rose-red to light pink colour. They

contain Fe 0·08, Mn 0·12, Mg 0·09, corresponding with $FeCO_3$ 0·17, $MnCO_3$ 0·25, $MgCO_3$ 0·32. Neodymium, to which the colour is attributed (A., 1917, ii, 209), is present in amounts too small for analytical recognition. L. J. S.

Latent Heat of Fusion of Cristobalite. E. W. Washburn (*J. Amer. Ceram. Soc.*, 1919, **2**, 1007—1008).—The author assumes that, in binary systems containing some alumina and a large proportion of silica, the solute exists in the form of molecules having simple molecular weights, and calculates the latent heat of fusion of cristobalite by means of the law regulating the lowering of the fusion point of dilute solutions, using the formula $L=RT^2/\Delta t \cdot x$, where L=the latent heat of fusion, R=the gas constant (2 cal.), T=the absolute melting point of cristobalite (1983° abs.) (1610° is the melting point of the eutectic for binary mixtures of alumina and silica containing 87 per cent. of silica and 13 per cent. of alumina), t=the lowering of the freezing point (1710—1610°), and x=the molar fraction of the solute.

Assuming the solute is sillimanite, Al_2SiO_5, L=6950 cal. per mol.: on the less probable assumption that the solute is alumina, Al_2O_3, L=6360 cal. per mol. Giving greater weight to the former assumption, the author suggests that the latent heat of fusion of cristobalite is 6800 cal. per mol. If the molecules of the solute are associated, and so ought to be represented by layer integers in the formulæ, the heat of fusion obtained by calculation in this manner is too large. A. B. S.

Fusion and Transition Phenomena of Spodumene. F. Meissner (*Zeitsch. anorg. Chem.*, 1920, **110**, 187—195).—The transition from α- to β-spodumene proceeds rapidly when the mineral is heated above 1000°. Experiments were made with the object of determining whether the transition is reversible. The spodumene was first heated for one and a-half hours at 900° to start the change into the β-form, and then samples, of varying degrees of fineness, were heated for varying periods at temperatures from 800° to 900°, the course of change being followed by density determinations. In every case the change into the β-form proceeded, no evidence of reversibility being obtained. The transition could be detected by optical means, in the case of thin cleavage plates, after heating for three hours at 720°, that is, 150° lower than the minimum temperature at which a change of density can be detected. In agreement with the work of Ballo and Dittler (A., 1912, ii, 758), no evidence of reversibility could be detected by thermal methods. The so-called γ-form of spodumene, which crystallises from the molten material, has been examined and compared with the β-form. In all probability the two forms are identical. The refractive indices are not appreciably different, and the difference between the melting points observed by the above authors (1380° for the β-form and 1290° for the γ-form) is probably due to the low fusion and crystallisation velocity of the substance. E. H. R.

Echellite, A New Mineral. N. L. BOWEN (*Amer. Min.*, 1920, **5**, 1—3).—This occurs as small, white, spheroidal masses of radiating fibres in a basic igneous rock at the Sextant portage, Abitibi river, northern Ontario. The optical characters point to orthorhombic symmetry; $\alpha=1{\cdot}530$, $\beta=1{\cdot}533$, $\gamma=1{\cdot}545$; positive. It is easily decomposed by hydrochloric acid. Analysis:

SiO_2.	Al_2O_3.	CaO.	BaO.	Na_2O.	K_2O.	H_2O.	Total.
34·5	40·0	7·2	nil	4·1	trace	14·4	100·2

gives the formula $(Ca,Na_2)O,2Al_2O_3,3SiO_2,4H_2O$. The name *echellite* (from French, *échelle*, ladder) alludes to the stepped ratios, 1, 2, 3, 4, in this formula. The ratio $CaO:Na_2O=2:1$. The mineral shows certain resemblances to the zeolites, but in the latter the ratio $Al_2O_3:(Ca,Na_2)O$ is nearly always 1:1. The formula is written in the form $(Ca,Na_2)Al(OH)_2Al_2(SiO_4)_3,3H_2O$ to show a relation to zoisite. L. J. S.

Zebedassite, a New Hydrated Silicate of Aluminium and Magnesium from Zebedassi in the Pavian Apennines. AMALIA BRUSONI (*Rend. R. Ist. Lombardo Sci. Lett.*, 1917, [ii], 50, 646—650; *Riv. Min. Crist. Ital.*, 1918, **50**, 74—79).—The mineral fills fissures in an altered rock found as loose blocks on a hill of serpentine at Zebedassi, near Volpedo. The rock (partial anal. I) has probably been derived from granite or gneiss. The new mineral forms white, fibrous aggregates with silky lustre. The fibres have straight optical extinction, and are probably orthorhombic: $n=1{\cdot}51$—$1{\cdot}53$, D 2·194, H 2. The mineral is easily soluble in acids with separation of gelatinous silica. Some water is lost over sulphuric acid, and between 105° and about 200° the loss is 2·40%. Analysis II of material dried at 105°:

	SiO_2.*	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O (over 105°).	Total.
I.	47·06	9·80	8·09	0·82	23·58	9·01	—
II.	50·27	12·90	—	—	26·98	10·49	100·64

In the earlier publication the formula is given as

$$9H_2O,2Al_2O_3,11MgO,13SiO_2,$$

but in the later it is written more simply as

$$4H_2O.Al_2O_3,5MgO,6SiO_2$$

or $H_8Al_2Mg_5(SiO_4)_6$. The mineral is near neolite. L. J. S.

Analytical Chemistry.

Analytical Weighing. Horace L. Wells (*J. Amer. Chem. Soc.*, 1920, **42**, 411—419).—The author advocates the use of the short swing method of weighing in place of the more tedious long swing method so often advocated in text-books. E. H. R.

A Nephelometer. Charles Chéneveau and René Audubert (*Compt. rend.*, 1920, **170**, 728—731).—The construction of the nephelometer is based on the formula $I/I_0 = 1 - e^{-BM^3}$, where I and I_0 are the intensity of the transmitted and incident light respectively and M the total mass of the particles in suspension in the medium. The absorption of the medium is compensated by a prism of very slight angle, of neutral tinted glass. It is shown that the displacement, x, of this prism for the compensation is a linear function of M, and consequently the value of M may be read off directly on a scale. [See, further, *J. Soc. Chem. Ind.*, 1920, 350A.] W. G.

Machine for Washing Precipitates. Eric Sinkinson (*Analyst*, 1920, **45**, 94—97).—The funnel containing the filter and precipitate to be washed is supported in a ring at one end of a counterpoised rocking arm; the latter is connected with a commutator to reverse a motor actuating the valve on the water supply. When the motor is started, the valve is opened and water is admitted through a rotating jet on to the precipitate. As soon as a certain weight of water has collected in the funnel, the rocking arm is depressed, the motor is reversed, and the valve closed. As soon as a sufficient quantity of water has passed from the funnel, the rocking arm rises, the motor is thus again reversed, and water admitted to the funnel, and so on. W. P. S.

New, Simple and Rapid Process for Collecting and Characterising the Films Produced by Metalloids and Metals capable of being Volatilised by Heat. Ad. Braly (*Compt. rend.*, 1920, **170**, 661—663).—A simple portable apparatus is described for use in the field by prospectors in the examination of minerals. It consists essentially of two plates of mica, suitably mounted, on one of which the mineral is heated in the blowpipe flame, the second being so adjusted as to condense and collect the resulting volatile vapours. To the film thus obtained the usual tests, for characterising the metals present, may be applied. By suitably regulating the flame temperature it is possible to obtain successive films from the different metals or metalloids present in the mineral. W. G.

The Titration of Mixed Acids by Conductivity Methods. I. M. Kolthoff (*Rec. trav. chim.*, 1920, **39**, 280—302).—For the most part, the results confirm the work of Meerburg (compare A.,

1919, ii, 518). It is not possible to estimate lactic acid in gastric juice by the conductivity method, although the total acidity of the juice may be readily determined by this method.

The method is suitable for estimating, with a very fair degree of accuracy, either small amounts of weak acids, such as acetic acid, mixed with larger amounts of strong acids, such as hydrochloric acid, or vice versa, and may be applied, therefore, to the estimation of mineral acids in vinegar. Weak bases may similarly be estimated in the presence of strong bases by the conductivity titration method. W. G.

A Simple, Rapid Method for the Estimation of Halogen in Organic Substances. W. A. Van Winkle and G. McP. Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 333—347).—A simple and accurate combustion method has been developed for the estimation of chlorine, bromine, or iodine in readily volatile organic compounds. The weighed material is volatilised with air from a specially designed sample holder, and is passed through a quartz tube heated for a length of about 25 cm. at 900—1000°. The products of combustion pass to an absorption apparatus containing an absorbing solution, prepared by mixing 25 c.c. of 5*N*-sodium hydroxide solution with 10 c.c. of 2*N*-sodium sulphite solution. The sulphite serves to reduce any oxy-halogen salts formed. The time taken for the combustion is from one to two hours. The excess of sulphite in the absorbing solution is then oxidised with potassium permanganate, and the halogen estimated by the Volhard process. The method was used for the analysis of ethyl bromide, ethyl iodide, ethylene chloride, bromobenzene, allyl bromide, chloroform, chloropicrin, and a number of other compounds, and gave results equal or superior to those given by the Carius method. With a slight modification of the apparatus, equally good results were obtained for less volatile substances, such as hexachlorobenzene, *m*-chloronitrobenzene, and *p*-bromoaniline. E. H. R.

Detection of Chloride in the Presence of Bromide. Carl Faurholt (*K. Danske Vidensk. Medd. Math. Phys.*, 1919, 2, No. 9, 1—16; from *Chem. Zentr.*, 1920, ii, 424).—Hager's method, which depends on the separation of the silver haloids from one another by taking advantage of their differing solubilities in ammonia and ammonium sesquicarbonate solution, is modified by the substitution of very dilute ammonia to which a little silver nitrate is added, in order to depress the solubility of silver bromide without sensibly altering that of silver chloride. Potassium nitrate is also added to prevent the possibility of the formation of colloidal solutions (0·25 mol. NH_3 + 0·01 mol. $AgNO_3$ + 0·25 mol. KNO_3 or 0·50 mol. NH_3 + 0·05 mol. $AgNO_3$ + 0·25 mol. KNO_3 per litre). H. W.

Chlorides in Water Analysis. E. Malmejac (*J. Pharm. Chim.*, 1920, [vii], 21, 263—268).—Results of analyses of various waters

are recorded, and attention is directed to the fact that the quantity of chlorine present affords a useful indication of the presence or absence of animal-polluting substances, especially when the normal chlorine content of the water is known. W. P. S.

Estimation of Chlorides in Whole Blood. J. HAROLD AUSTIN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1920, **41**, 345—348).—The protein is precipitated from the blood by picric acid, or by a mixture of picric and nitric acids. The protein-free filtrate is then treated with silver nitrate, a quantitative precipitation of the total chlorides being obtained. The final titration may be carried out by the Van Slyke-Donleavy process (A., 1919, ii, 239). J. C. D.

The Estimation and Kinetics of Hypoiodous Acid in Acid Solution. VICTOR COFMAN (*Bull. Soc. chim.*, 1920, [iv], **27**, 234—239).—Hypoiodous acid reacts almost instantaneously with phenolic compounds, giving stable iodo-compounds (compare T., 1919, **115**, 1040), and on this is based the method for estimating this acid in the presence of free iodine or other iodine compounds. To a known, suitable volume of the liquid under examination, potassium iodide is added, and, after acidifying, if necessary, the free iodine is titrated with standard thiosulphate. This operation is then repeated, but an excess of phenol is added before the potassium iodide. The difference in the amount of iodine found by these two titrations is a measure of the amount of hypoiodous acid present. An examination of the reversible action $2I_2 + HIO_3 + 2H_2O \rightleftharpoons 5HIO$ shows that the velocity of formation of hypoiodous acid is that of a bimolecular reaction. Similarly, measurements of the velocity of decomposition of the acid show that this change is also bimolecular. W. G.

Gravimetric Analysis. XII. Estimation of Sulphuric Acid. II. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 59—60).—Investigation of the precipitation of sulphuric acid as barium sulphate showed that when the acidity of the solution was reduced to $N/100$ by the addition of potassium carbonate or ammonia, the solution then boiled, treated with barium chloride solution, and the precipitate collected after eighteen hours, the weight of the precipitate, dried at 130° (about 0·3 gram), required to be multiplied by 1·0045 to obtain the correct weight. If the precipitate was ignited before being weighed, the factor was 1·0099. It was proved that the barium sulphate dried at 130° lost a small quantity of sulphuric acid when ignited. If sodium carbonate was used for the neutralisation of the sulphuric acid, the results obtained were not concordant. W. P. S.

The Kjeldahl Method for the Estimation of Nitrogen. I. K. PHELPS and H. W. DAUDT (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 218—220).—By using 0·7 gram of mercuric oxide, 10 grams of potassium sulphate and 25 c.c. of sulphuric acid, with

from 0·2 to 0·4 gram of substance, it was found that the Kjeldahl method was trustworthy for the estimation of nitrogen in the following compounds: glucosamine hydrochloride, isatin, atropine, cocaine, nicotinic acid, alkaloids, including caffeine, quinoxaline hydrochloride, 2-methyl-4-quinazolone, and 3-phenyl-2-methyl-4-quinazolone. The hydrolysis required 2·5 hours. W. P. S.

Use of Potassium Permanganate in Estimating Nitrogen by the Kjeldahl Method. WILLIAM FREAR, WALTER THOMAS, and H. D. EDMISTON (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 220—224).—In estimating nitrogen in a number of different fertilisers, there was a considerable loss of nitrogen when permanganate was added at the end of the acid digestion period; the extent of the loss depended on the amount of permanganate added, and more particularly on the time at which the addition was made. If the addition was delayed for two minutes after the burner had been removed, there was no loss of nitrogen.

W. P. S.

A Modification of the Apparatus for the Estimation of Arginine Nitrogen by Van Slyke's Method. GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 611—612).—A modified apparatus for the Van Slyke estimation of arginine consists of a Kjeldahl flask fitted with a cork, which carries a tap funnel for the addition of water at the end of the potassium hydroxide digestion, and the elongated, water-jacketed tube of a Kjeldahl still-head. This arrangement obviates loss of material by bumping, or of ammonia in the transference from one vessel to another, in the ordinary procedure. J. K.

Distillation of Ammonia. B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1920, **12**, 176—177).—For the distillation of ammonia in the estimation of nitric nitrogen (A., 1919, ii, 242), the most trustworthy results are obtained by the use of a condenser of block tin and the scrubber previously described (A., 1919, ii, 296). In using this apparatus with the ordinary Kjeldahl process, the following method of distillation removes the last traces of ammonia from the condenser without unduly increasing the volume of liquid in the receiving flask, which leads to hydrolysis of the indicator salt. The solution is slowly distilled for twenty minutes, so as to collect about 80 c.c. of distillate, the condenser then drained, and the distillation continued for another fifteen minutes. The receiver is then covered to prevent absorption of carbon dioxide, and the distillate cooled and titrated. C. A. M.

Volumetric Estimation of Ammonia in Blood. P. GERARD (*Compt. rend. Soc. Biol.*, 1919, 1186; from *J. Pharm. Chim.*, 1920, [vii], **21**, 236—237).—Ten c.c. of the blood are collected in potassium oxalate solution in a test-tube 22 cm. in depth, 10 c.c. of 29% sodium carbonate solution and 2 c.c. of octyl alcohol are added (the alcohol prevents excessive frothing), and air is aspirated

through the mixture at the rate of 3 litres a minute for about seventy minutes. The test-tube is connected with an absorption vessel containing a definite quantity of $N/100$-sulphuric acid, which absorbs the ammonia, and the excess of acid is titrated subsequently with sodium hydroxide solution, using methyl-orange as indicator. W. P. S.

Estimation of the Nitro-group in Aromatic Organic Compounds. T. Callan, J. A. Russell Henderson, and N. Strafford (*J. Soc. Chem. Ind.*, 1920, **39**, 86—88T).—Although the nitro-group in many organic compounds may be estimated by reduction with titanium trichloride solution, the excess of the latter being titrated subsequently, in the case of *a*-nitronaphthalene, *o*-nitroanisole, nitrotolyl methyl ether, and similarly constituted compounds, the results obtained are much too low, owing to the formation of chlorinated amines. If titanous sulphate is used in place of titanium trichloride, chlorination does not occur, and the results obtained are trustworthy. Methods involving the use of stannous chloride also possess the disadvantage that, in certain cases, chlorinated compounds are formed. A method depending on the reduction of the nitro group with zinc and hydrochloric acid, and titration of the amine with sodium nitrite solution, yielded trustworthy results with such compounds as chloronitrobenzene-*o*-sulphonic acid, nitroanisole, *p*-nitrotoluenesulphonic acid, etc. W. P. S.

The Acidimetric Estimation of Boric Acid. J. A. M. van Liempt (*Rec. trav. chim.*, 1920, **39**, 358—370).—Boric acid may be estimated electrometrically by measuring the hydrogen-ion concentration of the solution after successive additions of standard alkali, providing a suitable excess of either mannitol, glycerol, or lævulose is previously added. The volume of alkali added is plotted against the values of p_H, and the curve shows a very marked inflexion at the neutralisation point if sufficient of the polyhydric alcohol has been added. W. G.

Estimation of Available Oxygen in Sodium Perborate and in Perborate Soap Powders. H. Trickett (*Analyst*, 1920, **45**, 88—91).—Titration of the perborate with permanganate solution is not very trustworthy; the best results are obtained by adding a slight excess of the perborate solution to a definite quantity of $N/10$-permanganate solution acidified with sulphuric acid, and then titrating the excess with permanganate solution. The temperature of the solution should be about 15°, and the acidity 5% of sulphuric acid, calculated on the total volume. The gasometric method for the estimation of perborate by means of permanganate is untrustworthy. A gasometric method depending on the decomposition of the perborate with hypochlorite is described. The perborate solution is treated in a nitrometer with sodium hypochlorite solution, and the volume of oxygen measured after the mixture has been shaken for five minutes. This method

may be applied directly to perborate soap powders, and the results obtained agree with those yielded by the usual iodometric method.

W. P. S.

Estimation of Carbon. L. Lescœur (*J. Pharm. Chim.*, 1920, [vii], **21**, 257—263).—The organic substance is mixed in a covered silver crucible with a mixture consisting of equal weights of sodium nitrate and potassium nitrate, sodium hydroxide solution (free from carbonate) is added, the whole is dried, and then fused. After cooling, the mass is dissolved in water, ammonium chloride and calcium chloride are added, and the resulting calcium carbonate is collected, washed, and titrated with $N/1$-hydrochloric acid, using methyl-orange as indicator. [See, further, *J. Soc. Chem. Ind.*, 1920, May.] W. P. S.

Rapid Method for the Estimation of Carbon in Organic Mixtures, particularly in Urine. L. Lescœur and O. Dutrieux (*Compt. rend. Soc. Biol.*, 1919, **82**, 1417—1418; from *Chem. Zentr.*, 1920, ii, 427).—The specimen, containing 100—200 mg. of carbon, is heated in a suitable vessel, preferably a silver crucible provided with a lid and exit tube, with an excess of sodium hydroxide (about 50 c.c. of a N-solution), and 10 grams of a mixture of equal amounts of potassium and sodium nitrates until vapours are no longer evolved, and finally to redness for a short time. The product is dissolved in hot water, and the alkali carbonate formed is estimated titrimetrically. H. W.

Combustion by the Sulphochromic Mixture of Organic Compounds containing Chlorine. J. Guyot and L. J. Simon (*Compt. rend.*, 1920, **170**, 734—736).—The method of oxidation of methyl esters by a mixture of sulphuric and chromic acids (compare this vol., i, 284) has been extended to chloro-compounds with success. It is necessary to interpose between the reaction vessel and the gas burette, where the carbon dioxide is measured, an amalgamated spiral of copper to retain the chlorine. In addition, in some cases there is a tendency to form carbonyl chloride, but this can be overcome by using an excess of chromic acid.

Theoretical results were obtained with methyl chlorosulphonate and chloroformate, but in the case of the ethyl esters, the ethyl group did not readily undergo oxidation. It is of interest to note that, whereas acetic acid did not undergo oxidation by this method (*loc. cit.*), its chloro-derivatives are completely oxidised. This difference is confirmed by a comparison of the behaviour of hydrocarbons and their chloro-derivatives towards this oxidising agent. W. G.

Estimation of Mineral Constituents in Organic Substances, especially those containing Phosphorus. J. Grossfeld (*Chem. Zeit.*, 1920, **44**, 285—286).—The addition of magnesium acetate solution is recommended; after the mixture

has been dried, it is readily ignited, and the ash is free from unburnt carbon. Allowance must be made for the amount of magnesium oxide added as acetate. W. P. S.

Explosion during the Separation of Potassium by the Perchlorate Method. A. F. JOSEPH and F. J. MARTIN (*J. Soc. Chem. Ind.*, 1920, **39**, 94T).—To estimate sodium in a plant ash, the potassium was separated by precipitation as perchlorate, the filtrate and alcoholic washings (containing the sodium and excess of perchloric acid) were evaporated, and the sodium estimated as sulphate. On one occasion, when the alcoholic solution had been evaporated to a volume of a few c.c., violent explosion occurred. Possibly, some non-volatile substance derived from the alcohol reacted with the concentrated perchloric acid. W. P. S.

Estimation of Magnesium in Blood. W. DENIS (*J. Biol. Chem.*, 1920, **41**, 363—365).—The citrated plasma, serum, or whole blood is precipitated by three volumes of 6·5% trichloroacetic acid solution. The filtrate is used for the estimation of calcium, which is precipitated as oxalate by Lyman's method (A., 1917, ii, 271). The filtrate from the calcium is evaporated to dryness in a platinum dish with a small volume of 10% sulphuric acid and ignited over a free flame for two or three minutes. The cooled residue is dissolved in a small volume of distilled water, and the magnesium is precipitated as ammonium magnesium phosphate. An indirect estimation of the magnesium in this precipitate is then made by an estimation of the phosphate present by the nephelometric method with the strychnine molybdate reagent. J. C. D.

Estimation of Mercury by Glückmann's Method and Modifications of the same. ARTHUR ABELMANN (*Zeitsch. anal. Chem.*, 1919, **58**, 443—445).—The method (compare Peters, A., 1900, ii, 576) is liable to give untrustworthy results, owing to the solubility of mercury oxalate and the formation of basic salts, but this may be prevented by the addition of 2—3 c.c. of 5*N*-nitric acid to the mercury solution, using a large excess of oxalic acid for the precipitation, and introducing 50 c.c. of saturated potassium nitrate solution before the excess of oxalic acid is titrated with permanganate. W. P. S.

Estimation of Mercury in Organic Compounds. A. WÖBER (*Zeitsch. angew. Chem.*, 1920, **33**, 63—64).—The organic matter is destroyed by heating 0·5 gram of the substance with 5 c.c. of sulphuric acid in a flask fitted with a tapped funnel and a delivery tube connected with a Peligot tube cooled externally with water; 1 c.c. of concentrated hydrogen peroxide solution is added, drop by drop, through the funnel, and the heating is continued until sulphur trioxide fumes appear in the Peligot tube and a clear solution is obtained in the flask. The contents of the latter are then cooled, diluted, 1 gram of sodium chloride is added, the mix-

ture neutralised with sodium hydroxide, and, together with rinsings from the Peligot tube, diluted to 100 c.c. The mercury is estimated in this solution by the iodometric method described by Rupp (A., 1908, ii, 1073). W. P. S.

Detection of Manganese and Zinc in the Presence of Phosphates or Oxalates. H. WESTER (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 142—145; *Pharm. Weekblad*, 1920, **51**, 381—385).—In the presence of phosphates, manganese is precipitated as phosphate when its solution is treated with ammonia or ammonium sulphide; the precipitate does not dissolve in an excess of the reagents, and ammonium chloride does not prevent the precipitation. When oxalates, but not phosphates, are present, the manganese remains in solution when treated with ammonia, etc. Zinc is not precipitated by an excess of ammonia and ammonium chloride, even in the presence of oxalates and phosphates. W. P. S.

Gravimetric Estimation of Manganese in Iron Ores and in the so-called Manganese Ores. BALLOT (*Bull. Sci. Pharmacol.*, 1919, **26**, 514—516; from *Chem. Zentr.*, 1920, ii, 425).—The ore (0·25 gram, or 0·5—1 gram in the case of low manganese content) is fused with sodium peroxide in a nickel crucible. The cold, fused mass is dissolved in warm water (250 c.c.), and any manganate or permanganate is reduced by cautious addition of 95% alcohol. The filtered oxides of iron and manganese are dissolved by warming in a mixture of hydrochloric acid (10 c.c.), nitric acid (10 c.c.), and water (20 c.c.); the solution is treated with ammonia, diluted to 200 c.c., and heated to boiling. It is then treated with a suspension of barium carbonate in small quantities at a time until the supernatant liquor is no longer yellow. The precipitate is allowed to subside, and is then filtered. Excess of barium is removed from the combined filtrate and washings by means of ammonium sulphate, and the cold filtrate (which is diluted to 500—700 c.c.) is treated drop by drop with bromine until distinctly yellow in colour; ammonia is added in excess, and the mixture is heated to boiling. The precipitated manganese oxide is ignited and weighed as Mn_3O_4. H. W.

Volumetric Estimation of Manganese. PAUL NICOLARDOT, ANTOINE RÉGLADE, and MAX GELOSO (*Compt. rend.*, 1920, **170**, 808—810).—In using Knorre's method for the volumetric estimation of manganese, the manganese being precipitated by ammonium persulphate as the dioxide, and this precipitate redissolved in an excess of some reducing solution, which in its turn is titrated with standard permanganate, the theoretical factor for the calculation is 1 gram of iron $=0·4917$ gram of manganese. In practice, it is found that this factor varies, owing to slight variation in the composition of the manganese dioxide precipitate. These variations are shown to be due to the presence of iron, the factor being 0·498 in the absence of iron and 0·4929 in the presence of 40% of iron. The acidity of the solution in which the pre-

ipitation occurs also has some influence, as when there is above 0% of sulphuric acid the precipitation of the manganese is ncomplete. W. G.

The Gravimetric Estimation of Molybdenum as Sulphide. IAN STĚRBA-BÖHM and JAROSLAV VOSTŘEBAL (*Zeitsch. anorg. Chem.*, 1920, **110**, 81—103).—The difficulties attending the estimation of molybdenum as sulphide can be avoided if the precipitation is carried out in presence of formic acid and certain precautions are taken. In presence of mineral acids, or even acetic or oxalic acid, precipitation is incomplete, on account of the formation of colloidal solutions. The molybdenum must all be present as molybdate, and any trace of reduced molybdenum must be first oxidised by means of nitric acid. The following procedure is recommended for carrying out a determination. A quantity of solution is taken containing from 0·1 to 0·3 gram of molybdenum trioxide, and is diluted with water to 200—300 c.c. Sufficient formic acid is then added to give a 5% solution of free acid. If less than this quantity of formic acid is used, colloidal solutions of molybdenum sulphide are liable to be formed, but more acid is not detrimental. If only small quantities of electrolytes are present in solution, it is advisable to add a small quantity of pure potassium chloride, up to 0·75%, calculated on the total volume of the solution. Directly the formic acid has been added, a rapid stream of hydrogen sulphide, free from acid, is passed through the solution, for the first half hour in the cold and then for one to one and a-half hours at 40—50°. Alternatively, the hydrogen sulphide may be passed for two hours into an alkaline solution of the molybdate (alkaline with ammonia or potassium hydroxide), the formic acid then added, and the solution heated for one hour on the water-bath. The precipitated molybdenum sulphide is washed by decantation, filtered on a Gooch crucible, and dried in a current of carbon dioxide, first at 100°, then at 250°. It is then cooled in the current of gas and weighed, since it is hygroscopic, in a weighing bottle. The product obtained when these conditions are observed is shown to have the exact composition MoS_3.

The sulphide prepared as above has a brownish-black to chocolate colour. Heated in air at 126°, it oxidises considerably, and in a current of oxygen, oxidation takes place at a lower temperature with incandescence, but complete oxidation to MoO_3 is only brought about with difficulty. The freshly precipitated sulphide can be digested with cold concentrated formic acid for twenty-four hours without any appreciable quantity of molybdenum passing into solution. The most delicate test for traces of molybdenum is shown to be the stannous chloride–thiocyanate–ether test, by means of which 1 part of molybdenum in 625,000 parts of water can readily be detected. E. H. R.

[Reactions of Osmium Tetroxide]. C. A. MITCHELL (*Analyst*, 1920, **45**, 125—127).—It was shown by Schlüttig and Neumann (*Die Eisengallustinten*, 1890, 16) that to produce a permanent

coloration with iron salts (that is, an ink) a substance must contain three hydroxyl groups in juxtaposition. The same rule applies to the colour reactions of osmium tetroxide, which yields an ink with gallotannic and gallic acids and with pyrogallol, but not with phenol or quinol. In very dilute solution osmic pyrogallate is at first violet, but almost immediately becomes greenish-blue, and when applied to paper gives a deep violet-black coloration. The reaction affords a sensitive test for osmium tetroxide, the distinctive blue coloration being obtained on adding a trace of solid pyrogallol to a solution containing a few drops of 1% osmium tetroxide solution. The vapour from boiling "osmic acid" solution will develop recent finger prints on paper, and conversely a slightly greasy finger print affords a test for osmium tetroxide, traces of organic substances left by the finger giving permanent grey to black colorations owing to the reduction of the osmium tetroxide to osmium. C. A. M.

Estimation of Trimethylene Glycol in Distilled Glycerol (Dynamite Glycerin) and in "First Runnings." C. A. ROJAHN (*Zeitsch. anal. Chem.*, 1919, **58**, 433—442).—The quantity of trimethylene glycol present may be calculated from the water content and specific gravity of the sample. The water is estimated by drying 2 grams of the sample on asbestos under reduced pressure over phosphoric oxide. Tables and graphs are given, and reference to these gives the percentage of trimethylene glycol directly. [See, further, *J. Soc. Chem. Ind.*, 1920, 314A] W. P. S.

The Use of Aromatic Sulphochloroamides as Reagents. ALBERT BERTHELOT and M. MICHEL (*Bull. Sci. Pharmacol.*, 1919, **26**, 401—407; from *Chem. Zentr.*, 1920, ii, 425—426).—Neutral or alkaline solutions of sodium *p*-toluenedisulphochloroamide (chloramine-*T*) yield characteristic colorations, particularly with polyhydroxy-phenols and other substances of phenolic nature which, to a certain extent, depend on the concentration of the solutions, the quantity of reagents, the nature of the solvent, and the temperature, and, under definite conditions, are suitable for the characterisation of the individual substances. When, for example, 1 c.c. of a cold saturated solution of chloramine-*T* (about 15%) is treated with 4 c.c. of a 10% solution of the dihydroxybenzenes, a green coloration which becomes yellow is observed with resorcinol, whilst catechol gives an amethyst and quinol a currant-red coloration, which rapidly becomes brown; the effects are still noticeable at dilutions 1:10,000, 1:50,000, and 1:1000 respectively. α-Naphthol solution (1%, 4 c.c.) gives a violet shade in the cold, whilst β-naphthol gives no coloration in the cold, but an immediate brownish-red colour in boiling solution; the extreme dilutions are 1:50,000 and 1:100,000. Similar but less characteristic effects are produced by *p*-sulphodichloroaminobenzoic acid (halazone) in sodium carbonate solution and by *p*-toluenesulphodichloroamide (dichloramine-*T*) in dichloroethylene, which may be useful for the identification of substances insoluble in water. H. W.

Detection and Characterisation of Dextrose in Plants by a New Biochemical Method. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, **170**, 631—635).—It has previously been shown (compare A., 1913, i, 542) that 82·6% of the dextrose in solution in 70% methyl alcohol is converted by emulsin into β-methyl glucoside. It is now shown that this change occurs in the presence of other sugars, such as mannose, lævulose, or arabinose, and the glucoside can be isolated in a crystalline form from the solution. This method can be used for the detection and estimation of dextrose in plants as follows. The dry plant material is extracted with boiling 80% alcohol, and the extract is evaporated to dryness. The residue is extracted with boiling ethyl acetate to remove resinous matters, and the residue is dissolved in a little water, and this solution is evaporated to dryness under reduced pressure. This final residue is dissolved in 70% methyl alcohol, and after the reducing power and rotation of the solution have been measured, emulsin is added and the liquid is left until no further change in the rotation occurs. The reducing power and rotation are again determined, and from these changes the amount of dextrose present in the original plant material can be calculated, allowing for 82·6% of it having been converted into β-methyl-glucoside. If required, the glucoside may be isolated from the methyl-alcoholic solution. W. G.

A System of Blood Analysis. Supplement I. A Simplified and Improved Method for the Estimation of Sugar. OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1920, **41**, 367—374). —In the method previously described (A., 1919, ii, 308) an error due to phenols is present. The authors now describe the preparation of a modified reagent, which gives no colour with phenols, but reacts with cuprous copper in acid solution. The criticisms which have been levelled at these methods on the grounds of reoxidation are discussed, and a special type of sugar tube is described, use of which prevents this source of error. The method is now considered to be without flaw. J. C. D.

Double Polarisation Methods for the Estimation of Sucrose, and a Suggested New Method. GEO. W. ROLFE and L. F. HOYT (*J. Ind. Eng. Chem.*, 1920, **12**, 250—253).—The rotatory power before inversion is determined on clarified solutions containing 3% of monochloroacetic acid, within fifteen minutes of the addition of the acid, no inversion occurring within this period at the ordinary temperature. A portion of the solution is then heated in a tightly stoppered flask for thirty minutes in boiling water, and the rotatory power is determined after the cooled solution has been kept for at least two hours. When the Ventzke sugar scale is used the sucrose is calculated by the usual Herzfeld formula with the substitution of 141·0 for the Herzfeld inversion constant. The results agree well with those obtained by the use of invertase as hydrolyst. [See also *J. Soc. Chem. Ind.*, 1920, May.] J. H. L.

Colorimetric Estimation of Glycogen. R. Thieulin (*J. Pharm. Chim.*, 1920, [vii], **21**, 91—93).—Two c.c. of the neutralised glycogen solution are treated with two drops of iodine solution (iodine 1 gram, potassium iodide 2 grams, water 20 c.c.), and the reddish-brown coloration obtained is compared with those given by known amounts of glycogen under the same conditions.

W. P. S.

Specific Colour Reaction of Oxalates. V. Macri (*Boll. Chim. Farm.*, 1920, **59**, 73).—The colour reaction for oxalates described by Caron and Raquet (A., 1919, ii, 438) was published earlier by the author (A., 1917, ii, 511) as a reaction for detecting manganese salts. The author now finds that addition of an oxidising agent, such as a hypochlorite, a dichromate, or hydrogen peroxide, is unnecessary, since agitation of a solution of a manganese salt in the hot with a little alkali hydroxide causes absorption of atmospheric oxygen and formation of higher oxides of manganese, these giving the characteristic red coloration with an oxalate. The reaction does not take place in acid solutions. T. H. P.

Approximate Estimation of Acetone and Acetoacetic Acid when present together in Urine. Emil Lenk and Walther Hahn (*Münch. med. Woch.*, 1917, **64**, 179; *Zentr. Biochem. Biophys.*, **19**, 262).—The Légal test was used for the detection of acetone and acetoacetic acid collectively and the Rimini ethylenediamine test for the detection of acetoacetic acid alone. The colours obtained in both tests diminished in intensity very rapidly. In applying the reactions the pigment solutions were diluted with water until the liquid was colourless. Strongly coloured samples of urine must first be decolorised. Directions for performing the tests, together with tabulated data, are given.

Chemical Abstracts.

A New Manometric Ureometer. Paul Bobay (*J. Pharm. Chim.*, 1920, [vii], **21**, 62—64).—A description is given of a new ureometer, the two principal features of which are a piston with a ground surface fitting into the base of the ureometer and the addition of a manometric tube to the graduated tube. The apparatus is figured in the original, and a detailed account of its structure and method of manipulation is given. W. G.

Estimation of Urea in Blood. A. Slosse (*Compt. rend. soc. biol.*, 1919, **42**, 1402—1404; from *Chem. Zentr.*, 1920, ii, 427).—Comparative estimations by Folin's and the hypobromite method gave practically always discordant results. Hypobromite not only decomposes urea, but also other nitrogenous substances of the blood, uric acid, creatine, creatinine, and amino-acids, which are invariably present, and, in pathological cases, frequently in such quantity that they cannot be neglected. The errors which can arise in the calculation of Ambard's constant from such data are particularly considered. H. W.

New Colour Reactions of Quinine. D. GANASSINI (*Il policlinico*, 1917, **24**, 344; *Arch. ital. biol.*, 1919, **69**, 73).—A yellow coloration, which becomes rose and finally purplish-red, is developed when a few drops of pyridine are added to a solution of quinine or of a quinine salt containing a slight excess of freshly prepared chlorine water. The colouring matter is almost insoluble in chloroform. Quinidine and euquinidine respond very feebly to the test; cinchonine and cinchonidine are inert.

The green coloration developed in the thalleoquinine test with bromine water and the minimal amount of ammonia becomes red after the addition of one or two drops of a freshly prepared 0·1% solution of potassium ferricyanide. The colouring matter is extracted by chloroform. CHEMICAL ABSTRACTS.

Indican in the Liquids of Organisms and its Investigation for the Identification of Urine. LEONE LATTES (*Arch. Farm. sper. Sci. aff.*, 1919, **28**, 5—16, 17—22).—The detection of indican (indoxyl) in a spot forms a good, practical means for identifying urine, although theoretically the reaction is not absolutely specific. The reaction answers even when the spot has undergone putrefactive and similar changes. Failure of the reaction does not, however, exclude urine, since the spot may have experienced accidental alteration, besides which some urines may be either very poor in, or quite free from, indoxyl. T. H. P.

Estimation of Hæmoglobin by the Acid Hæmatin Method. LOUIS BERMAN (*Arch. Intern. Med.*, 1919, **24**, 553—556). —The Sahli method is modified by the use of a standard prepared daily, the use of 0·1*N*-hydrochloric acid as a diluent throughout, and heating the test to boiling for one minute after the first matching to accelerate and complete the reaction, after which the final dilution and reading are made. CHEMICAL ABSTRACTS.

A Comparative Study of Various Methods for the Estimation of Hæmoglobin. FRIEDA S. ROBSCHEIT (*J. Biol. Chem.*, 1920, **41**, 209—225).—When in Sahli's method the colour tubes accompanying the instrument are used, very inaccurate results may be obtained because of the decided variance in colour density of the standard tubes, due to fading. Palmer's method (A., 1918, ii, 88) is good, provided the standard solutions are freshly prepared, whilst Newcomer's method (A., 1919, ii, 179) gives good results with the glass 0·96 mm. in thickness. With the heavier glass, 1·02 mm. in thickness, the colour match is only approximate. A method is presented which applies Palmer's procedure to Sahli's principle. The standards for this process remain unappreciably changed for eleven months. J. C. D.

Estimation of Methæmoglobin in Blood. WILLIAM C. STADIE (*J. Biol. Chem.*, 1920, **41**, 237—241).—The method depends on the fact that both hæmoglobin and methæmoglobin are changed quantitatively into cyanohæmoglobin by dilute solutions of potassium

cyanide. The colour of the latter substance is a brilliant orange-red, and is very suitable for colorimetric comparison. The total amount of the hæmoglobin and methæmoglobin is estimated by this colorimetric method, whilst the hæmoglobin is determined separately from the oxygen capacity, employing Van Slyke's method for the gasometric estimation of that pigment. J. C. D.

The Detection of Blood in Fæces. P. N. VAN ECK (*Pharm. Weekblad,* 1920, **57**, 218—227).—A critical discussion of the methods which have been proposed. A bibliography of the subject is appended. W. S. M.

Benzidine as Chromogen in Biological Oxidation Reactions. M. KJÖLLERFELDT (*Pflüger's Archiv,* 1918, **172**, 318—334).—The value of benzidine hydrochloride solutions for these tests is dependent on the method of preparation, and on the age of the solution. The author recommends a *N*/200-solution of the pure hydrochloride as giving the best results. J. C. D.

Volumetric Estimation of the Alkalinity of Blood; Influence of Protein Substances on this Estimation. Its Value. RENÉ CLOGNE (*J. Pharm. Chim.*, 1920, [vii], **21**, 49—62).—The method recommended is as follows. Five c.c. of the blood or serum are introduced into a 50 c.c. graduated flask and diluted to 40 c.c. with a saturated solution of sodium chloride. The mixture is heated on a boiling water-bath, and to it 6 c.c. of *N*/10-nitric acid are added. After three minutes the liquid is cooled and made up to the mark with more sodium chloride solution and filtered. Forty c.c. of the filtrate are titrated with *N*/10-sodium hydroxide solution, using phenolphthalein as an indicator. The average of the results obtained from the blood of fourteen normal individuals, very slightly wounded, was an alkalinity equivalent to 3·17 grams of sodium hydroxide per litre. The average for ten men suffering from severe shock was 2·79 grams per litre, and for eight men severely wounded and suffering from gas gangrene was 2·86 grams per litre.

Further investigation showed that the results obtained depended, to a considerable extent, on the amount of *N*/10-acid added, the variations obtained being due to the presence of protein. The results obtained with a solution of egg-albumin and with blood serum indicate that the alkalinity results are probably a function of the protein present rather than of the alkaline bases. W. G.

Apparatus for Measurement of Oxydase and Catalase Activity. R. B. HARVEY (*J. Gen. Physiol.*, 1920, **2**, 253—254).—A description of a modified Bunzel apparatus (A., 1914, ii, 508). The source of error in the earlier forms of apparatus is a failure to absorb carbon dioxide which is produced. This error is removed in the new design by using an alkali hydroxide tube. J. C. D.